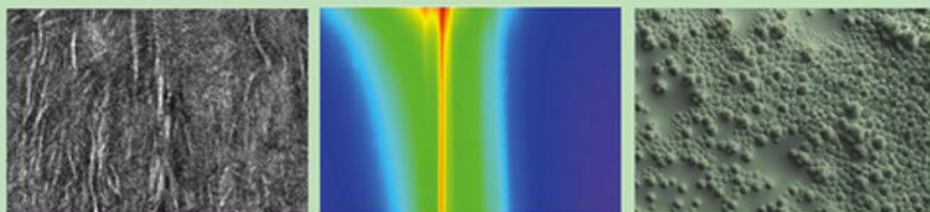


**Wiley Series on Polymer Engineering
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Polyurethanes

Science, Technology,
Markets, and Trends

Mark F. Sonnenschein

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POLYURETHANES

Science, Technology, Markets, and Trends

MARK F. SONNENSCHN, Ph.D.

The Dow Chemical Company
Midland, MI, USA

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*Dedicated to my wife Geraldine Franklin Sonnenschein for her beauty, kindness,
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CONTENTS

Acknowledgments	xi
1 Introduction	1
2 Polyurethane Building Blocks	10
2.1 Polyols, 11	
2.1.1 Polyether Polyols, 12	
2.1.2 Polyester Polyols, 28	
2.1.3 Other Polyols, 42	
2.1.4 Filled Polyols, 48	
2.1.5 Seed Oil-Derived Polyols, 53	
2.1.6 Prepolymers, 59	
2.2 Isocyanates, 61	
2.2.1 TDI, 63	
2.2.2 Diphenylmethane Diisocyanates (MDI), 73	
2.2.3 Aliphatic Isocyanates, 81	
2.3 Chain Extenders, 89	
3 Introduction to Polyurethane Chemistry	105
3.1 Introduction, 105	
3.2 Mechanism and Catalysis of Urethane Formation, 107	
3.3 Reactions of Isocyanates with Active Hydrogen Compounds, 113	

3.3.1	Urea Formation, 116	
3.3.2	Allophanate Formation, 117	
3.3.3	Formation of Biurets, 119	
3.3.4	Formation of Uretidione (isocyanate dimer), 119	
3.3.5	Formation of Carbodiimide, 120	
3.3.6	Formation of Uretonimine, 120	
3.3.7	Formation of Amides, 123	
4	Theoretical Concepts and Techniques in Polyurethane Science	127
4.1	Formation of Polyurethane Structure, 128	
4.2	Properties of Polyurethanes, 137	
4.2.1	Models and Calculations for Polymer Modulus, 138	
4.2.2	Models for Elastomer Stress Strain Properties, 143	
4.2.3	The Polyurethane Glass Transition Temperature, 152	
5	Analytical Characterization of Polyurethanes	160
5.1	Analysis of Reagents for Making Polyurethanes, 161	
5.1.1	Analysis of Polyols, 161	
5.1.2	Analysis of Isocyanates, 166	
5.2	Instrumental Analysis of Polyurethanes, 168	
5.2.1	Microscopy, 169	
5.2.2	IR Spectrometry, 176	
5.2.3	X-Ray Analyses, 181	
5.3	Mechanical Analysis, 188	
5.3.1	Tensile, Tear, and Elongation Testing, 189	
5.3.2	DMA, 195	
5.4	Nuclear Magnetic Spectroscopy, 199	
6	Polyurethane Flexible Foams: Chemistry and Fabrication	207
6.1	Making Polyurethane Foams, 208	
6.1.1	Slabstock Foams, 208	
6.1.2	Molded Foams, 213	
6.2	Foam Processes, 217	
6.2.1	Surfactancy and Catalysis, 223	
6.3	Flexible Foam Formulation and Structure–Property Relationships, 228	
6.3.1	Screening Tests, 228	
6.3.2	Foam Formulation and Structure–Property Relationships, 230	
7	Polyurethane Flexible Foams: Manufacture, Applications, Markets, and Trends	235
7.1	Applications, 237	
7.1.1	Furniture, 238	
7.1.2	Mattresses and Bedding, 241	

7.1.3	Transportation, 245	
7.1.4	The Molded Foam Market, 246	
7.2	Trends in Molded Foam Technology and Markets, 249	
8	Polyurethane Rigid Foams: Manufacture, Applications, Markets, and Trends	255
8.1	Regional Market Dynamics, 255	
8.2	Applications, 260	
8.2.1	Construction Foams, 260	
8.2.2	Rigid Construction Foam Market Segments, 272	
8.2.3	Appliance Foams, 276	
8.3	Blowing Agents and Insulation Fundamentals, 281	
8.3.1	Blowing Agents, 281	
8.3.2	Blowing Agent Phase-Out Schedule, 282	
8.4	Insulation Fundamentals, 284	
8.5	Trends in Rigid Foams Technology, 287	
9	Polyurethane Elastomers: Manufacture, Applications, Markets, and Trends	294
9.1	Regional Market Dynamics, 295	
9.2	Applications, 298	
9.2.1	Footwear, 300	
9.2.2	Nonfootwear Elastomer Applications and Methods of Manufacture, 307	
9.3	Trends in PU Elastomers, 328	
10	Polyurethane Adhesives and Coatings: Manufacture, Applications, Markets, and Trends	336
10.1	Adhesive and Coating Industries: Similarities and Differences, 336	
10.2	Adhesives, 339	
10.2.1	Adhesive Formulations, 342	
10.2.2	Trends in PU Adhesives, 350	
10.3	Coatings, 353	
10.3.1	PU Coating Formulations, 359	
10.3.2	Trends in PU Coatings, 368	
11	Special Topics: Medical Uses of Polyurethane	375
11.1	Markets and Participants, 375	
11.2	Technology, 377	
11.2.1	Catheters, 377	
11.2.2	Wound Dressings, 380	
11.2.3	Bioabsorbable Polyurethanes, 382	

- 11.2.4 Hydrogels, 386
- 11.2.5 Gloves and Condoms, 387

12 Special Topic: Nonisocyanate Routes to Polyurethanes 392

- 12.1 Governmental Regulation of Isocyanates, 392
- 12.2 Nonisocyanate Routes to Polyurethanes, 395
 - 12.2.1 Reactions of Polycyclic Carbonates with Polyamines, 395
 - 12.2.2 Direct Transformations of Amines to Urethanes, 400
 - 12.2.3 Reactions of Polycarbamates, 403
 - 12.2.4 Conversion of Hydroxamic Acids to Polyurethane, 404
 - 12.2.5 Conversion of Hydroxylamines to Polyurethanes, 406

Index 409

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1

INTRODUCTION

In the early 1900s, there were very few of the synthetic polymers we have grown accustomed to now. During succeeding years, polymer science experienced explosive growth with the invention of polyvinyl chloride (PVC, 1913), polyethylene (1933), polyvinylidene chloride (Saran, 1933), polyamides (nylon, 1934), and polytetrafluoroethylene (Teflon, 1938). In addition, during the 1930s, the polymer family known as polyurethanes was invented. Now, of course, polyurethanes, and all the polymers developed during this period, have become an integral part of modern life. As you read this, you may not be aware of how many ways polyurethanes surround you. They are present in the shoes you stand in, the seat cushion you sit upon, the carpet backing and foam pad underlay you walk upon, the fibers of your clothing, insulation of your walls and roof, your refrigerator, dishwasher, water heater, automotive seating, automotive structural foam, automotive paints and coatings, furniture coatings, your bed mattress, and the adhesive holding this book together—the list just goes on. This book's purpose is to explain polyurethane science, technology, applications, trends, and markets in virtually all of its forms and relate those structures to the properties that make them so suited for so many uses. It is not an overstatement to say that polyurethanes are, if not *the* most versatile class of materials, then certainly one of the most versatile polymer categories in existence.

Discovery of polyurethane chemistry is attributed to the efforts of Otto Bayer and the research team he led at the now defunct I.G. Farben AG chemical company. The first patent associated with polyurethanes was filed in 1937, and numerous other patents, most notably the production of flexible foams resulting from isocyanate–water reactions,

were filed thereafter. I.G. Farben was broken up following World War II for complicity in war crimes, and the company's top leaders were convicted for crimes against humanity (exploitation of slave labor and production of nerve gas). The largest surviving components of I.G. Farben, Bayer AG and BASF SE, remain very large and respected global chemical concerns and very large producers of polyurethane chemicals.

After the initial discovery and expositions of basic chemistry, mostly based on short-chain diols and polyester polyols, industrial polyurethanes saw immense growth following the development of polyether polyols by E.I. DuPont de Nemours and Co. and The Dow Chemical Co. While Dow Chemical remains one of the world's largest manufacturers of polyurethane chemicals, DuPont has exited its polyurethane businesses that were primarily textile and coating related. While polyesters remain prominent components of polyurethane chemistry, it was the superior processing, low-temperature flexibility, and hydrolytic stability of polyether polyols that expanded polyurethane polymers into their current acceptance in every aspect of modern life.

As ubiquitous as polyurethanes are, it is perhaps surprising that they represent a relatively minor (but still significant) fraction of the overall volume of plastics global consumption (Fig. 1.1). Structures of the listed commodity polymers are relatively simple repeating units (Fig. 1.2). Their simplicity is in part responsible for their high level of utility and low-cost positions. The plastics industry has generated variants of the structures shown in Figure 1.2 by introducing branching, for instance, but those complexities do not fundamentally alter the basic polymer structure.

Polyurethane is the largest volume commodity polymer that cannot be characterized by a simple structure such as shown in Figure 1.2. Instead, polyurethane represents a class of polymers, and *any* polymer with a urethane repeat unit is classified as a polyurethane regardless of the other functional or polymer structures incorporated (Fig. 1.3).

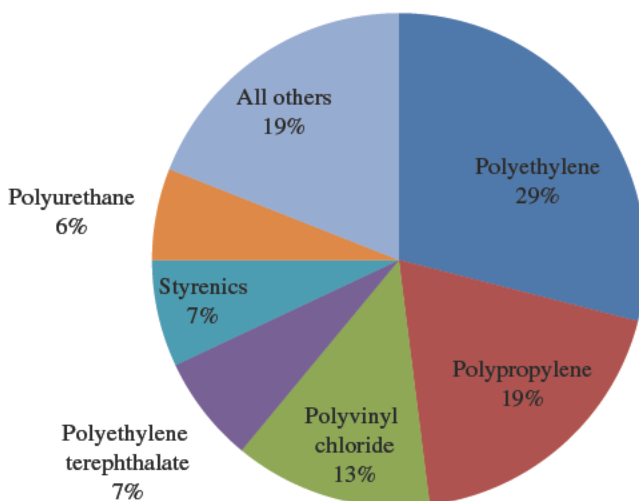


FIGURE 1.1 Percentage global consumption of plastics in 2012. Polyethylene encompasses all densities; styrenics includes all copolymers along with atactic polystyrene.

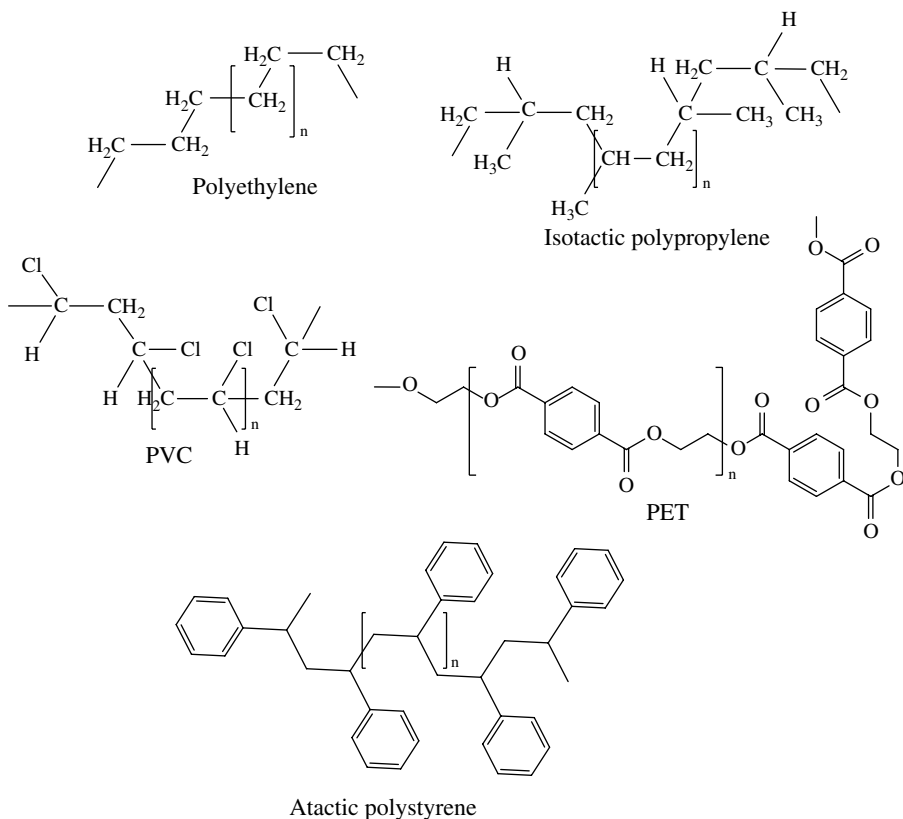


FIGURE 1.2 Illustrative structures of high volume commodity polymers.

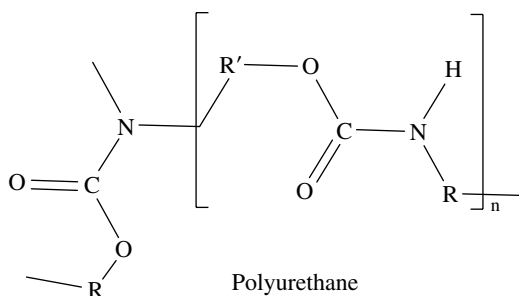


FIGURE 1.3 The urethane unit within a polyurethane polymer chain.

Specific polyurethane structures used for making mattress foam, or insulation foam, or shoe foam, can be significantly different from one another and cannot be neatly represented like the structures in Figure 1.2. In fact, even structures of different insulation foams can vary so widely that they also cannot be easily represented by a single structure. Another difference with other commodity polymers is that large

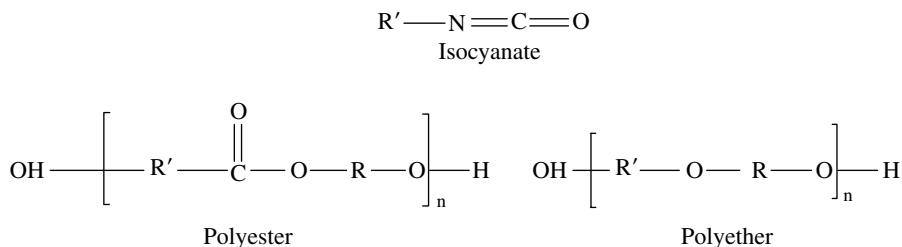


FIGURE 1.4 Chemical structures of isocyanate, polyester, and polyethers. To make a polyurethane, the R' of the isocyanate structure must also have an isocyanate function. Reprinted with permission from Ref. [1]. © John Wiley and Sons, Inc.

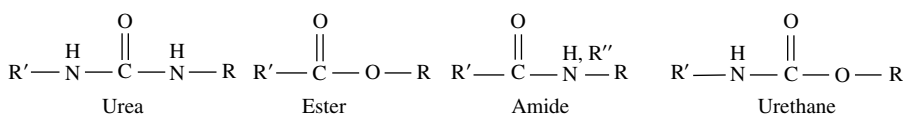


FIGURE 1.5 Structures of urea, ester, amide, and urethane functionalities.

volume polyurethane applications require the mixing of two reactive liquid components rather than the processing of a pellet into a molded or extruded object. Given these complexities, it is remarkable that polyurethanes have developed into a commodity plastic category and is a testament to polyurethane versatility and performance that polyurethanes are so difficult to replace in their favored applications.

Polyurethane polymers as a class are made from commodity building block reagents and short-chain polymers (or oligomers). These building blocks include categories: polyisocyanates, polyethers, polyesters, water, and amines, for example (Fig. 1.4). As building block categories, they also cannot be represented by unique structures and are denoted “R” to allow designers to insert any conceivable chemically allowable unit.

The polyurethane unit is easily mistaken for the related polyester, polyurea, or polyamide (nylon) structures (Fig. 1.5). In fact, polyureas, polyesters, and polyurethanes are often joined into polyurethane materials and still broadly classified as polyurethane (polyamides are not a part of polyurethane chemistry due to vastly different processing characteristics).

As commodity products, polyurethanes have achieved a certain establishment status in academic science. However, activity in polyurethane science shows no sign of abating, due to its high potential for design and innovation [1–14]. Figure 1.6 shows total global publication activity including patents, journal articles, reviews, meeting abstracts, governmental documents, etc. for the years 2003–2014 for all commodity plastics named in Figure 1.1. While many plastics exhibit activity approximately in proportion to their production, polyurethane activity is more than double its production. Figure 1.7 shows the annual growth of polyurethane publishing for publications where a polyurethane polymer *property* is the focus of the document. The steady growth of activity appears independent of general global economic activity. Figure 1.8 quantifies the kinds of publications over this time period showing that open literature publications predominate but that patent activity is nearly as prevalent.

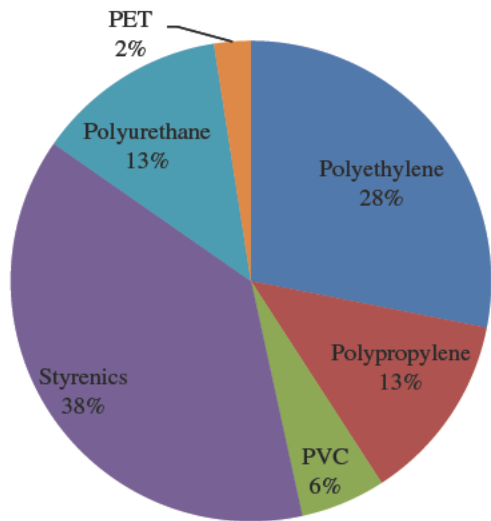


FIGURE 1.6 Publication activity focused on commodity plastics for the years 2003–2013. The total includes all public literature, patent filings, conference proceeding, and books where the subject focus is the plastic. The total number of publications for all listed plastics = 1,265,554.

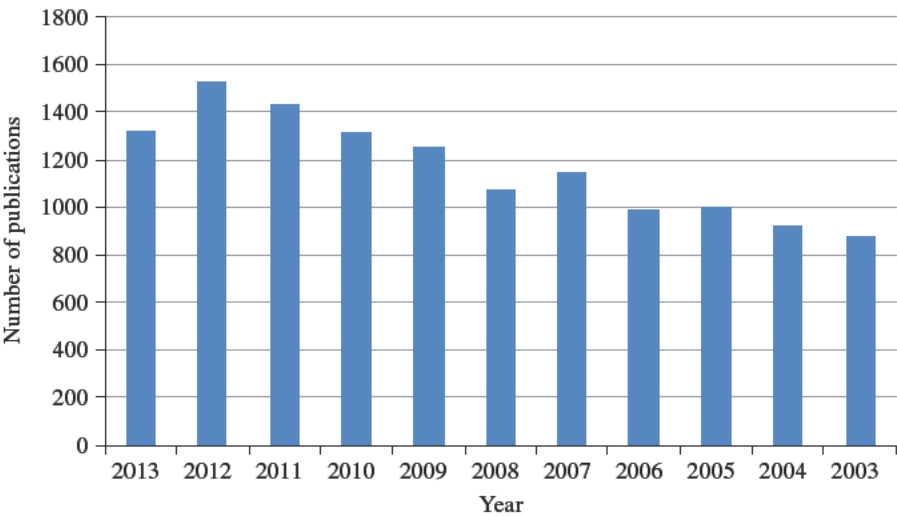


FIGURE 1.7 Publication activity for the years 2003–2013 where the subject focus is polyurethane polymer properties. Graph shows steady increase and no apparent dip in the global recession years 2008–2010. Only publications in English are collated. Addition of other languages does not materially change the distribution but does change the number.

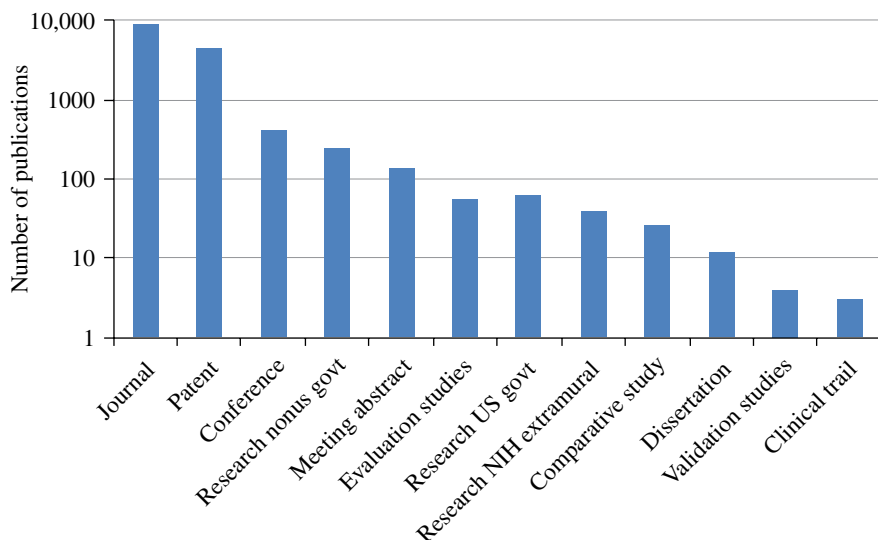


FIGURE 1.8 Type of publications where the focus of the work is polyurethane polymer properties for the years 2003–2013. The high level of open literature and patent activity demonstrates the continuing intellectual and commercial interest in these materials. The logarithmic scale may exaggerate the importance of items at the low end of the distribution. Only publications in English are collated, which partially skews the distribution. Addition of other languages would include a significant amount of work in Chinese.

This book also covers markets and commercial aspects of the polyurethane industry. The market and commercial activities overlap, but they are not synonymous. The overlap in how the words “marketing” and “commercial” are used reflects their conflation in meaning. Polyurethane market concepts are broader, more strategic, and more theoretical than commercial concepts. Marketing encompasses the equilibrium and nonequilibrium driving forces that make one material attractive to a consumer and another unacceptable. They take into consideration regional preferences, regional access to feedstocks, and the underlying cultural and societal influences that make a product useful or desirable or possess value. They also include the advantages a particular competitor in a market may possess from all facets including intellectual (i.e., patents).

The commercial aspects of an industrial product include those aspects that are important to specific customers or groups of customers such as advantages or value a product may have versus a competitive material or a competitive company. Probably the most prominent commercial aspect, especially for commoditized products, is price and price movement. Without doubt, thorough and confident knowledge of pricing in commerce is essential and can distinguish a profitable enterprise from one that fails. A commercial move to raise prices when there is excess capacity, or failure to raise prices when there are shortages or feedstock prices are rising, is common commercial failure, and the ability to shrewdly navigate price movements is the hallmark of well-run companies.

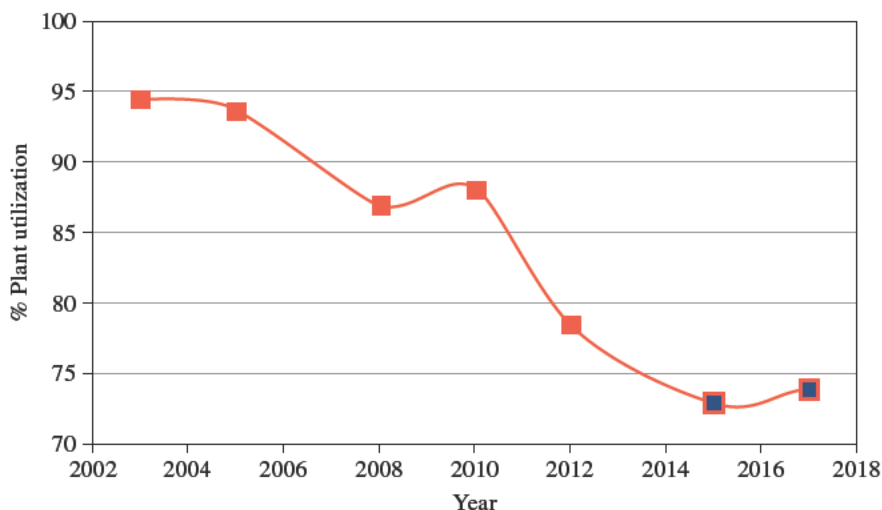


FIGURE 1.9 Percentage isocyanate plant capacity utilization. Projections are indicated by enhanced data points based on announced capacity increases and closings and growth extrapolations.

In recent years, the polyurethane industry has been subject to significant macroeconomic forces. The overriding force has been the expansion of polyurethane feedstock manufacturing capacity in China. In particular, this capacity growth has injected chemical production during a period of global economic stagnation (especially in Europe) and slow growth environments in North America. Figure 1.9 shows the extent of isocyanate overproduction. The deteriorating demand/capacity ratio can have a very material impact on price expectations and influence decisions on additional capacity expansions. It is not always the case that manufacturers flee a market in response to temporary price declines resulting from overexpansion. It has occurred in the past that manufacturers with a strong financial base will wait out the failure of financially weaker producers. The closure of these weak assets will reduce production volumes, called “tightening the market.” It has also occurred in the past that manufacturers with a particularly strong financial position and a strong commitment to the market will increase production in the face of overcapacity to further drive down prices and drive weak manufacturers into untenable production economics. The anticipated response is for weak producers to shutter poorly performing manufacturing assets or sell their business to one of their competitors. Following these closings, production can regain a capacity/demand balance and prices can rise. This kind of “game” is not seen very often now in the chemical industry. In part, this is due to the relatively small number of global manufacturers and their similar financial strengths, maturity, and experience. Additionally, regulation of monopolistic behavior has become more stringent, and the potential gain by this kind of predatory practice may not be worth the potential reputational risk. Lastly, many manufacturers see the

benefit of strong and rational competition in the marketplace. Rational and mature competition can provide ballast to minimize market fluctuations and provide a stimulus to improve business performance. In contrast to rational industrial practices, the recent haphazard expansion of polyurethane elastic fiber production has witnessed rapid capacity expansion concomitantly with falling prices. Very few major manufactures from the year 2000 are still in the market, and commercial profitability and market value have probably been permanently destroyed. This is covered in detail in Chapter 9.

The trends in polyurethane manufacturing reflect global competitive pressures and global opportunities. This has resulted in expansion of manufacturing assets close to raw material feedstocks and also close to geographies with increasing economic growth. It is not immediately clear whether it is cheaper to ship commodity feedstocks to centers of economic activity or ship finished polyurethane chemicals from low-cost manufacturing sites. However, low feedstock cost manufacturing is probably less prone to geopolitical factors and will always maintain a low-cost position. On the other hand, market and commercial flexibility is enhanced by proximity to customers.

There is continuing movement toward manufacturing innovation using processes that reduce usage of solvents and reagents and involve less purification and environmental impact. There is probably little incentive for production of new families of polyurethane building blocks, particularly for new polyisocyanates. It would appear that the regulatory burden of new isocyanate production inhibits innovation, and currently available products perform adequately and at acceptable cost. In the same regard, there has been relatively weak growth of polyols derived from new DMC catalysts despite the performance advantages of the polyol product (see Chapter 2). Again, this is probably due to insufficient performance/cost incentive for manufacturers or customers resulting in slow adoption. On the other hand, improvements in established products, such as production of copolymer polyols with ever higher solid content, lower viscosity, and smaller particle size, will undoubtedly continue and find success in the market.

The trend for polyurethane applications is being driven by overriding trends in the industries in which polyurethanes find purpose. Thus, automotive trends toward lighter weight dictate a trend toward higher performance at lower foam density. Higher performance includes achieving required comfort factors with lower vibration and noise transmission. In construction markets, the trend is toward improved thermal insulation with new blowing agents that exhibit lower ozone depletion potential and now lower global warming potential as well. Restrictions on acceptable flame retardant packages for both flexible foams and rigid foams are also a driver of polyurethane industrial innovation. Thus, blowing agents and flame retardants score highly in the intensity of industrial activity associated with polyurethanes. Industrially, reactive catalyst innovation has been consistently pursued (to reduce fugitive catalyst emissions). This trend may intensify in the future due to governmental and consumer pressures, particularly in Europe. The trend toward further employment of renewable feedstocks has been slow and based on patent activity will probably remain so for the near future.

The science of polyurethanes is ongoing and will continue a high level of activity in the future. While a great deal is known about the fundamentals of polyurethane

structure–property relationships, the control of these relationships is still being actively pursued. Most understanding of polyurethanes is based on equilibrium properties; however, due to kinetic limitations of reaction-induced phase separation, theory and reality are often in conflict. Exponential increases in computing power allow for finer-grained simulations of larger volumes that can be harnessed by modern self-consistent field theoretical techniques to better predict or simulate experimental results.

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2

POLYURETHANE BUILDING BLOCKS

The versatility of polyurethanes is derived in large part from the wide selection of building blocks available to materials designers. The growth of polyurethanes has been highly dependent on the cheap and available feedstock polyisocyanates, polyols, and chain extender coreactants such as water, alcohols, and amines. However, this paradigm has recently been challenged as substitutions are made for purposes of avoiding health and safety issues associated with isocyanates. A detailed discussion of substitute chemistries to urethane structures will be handled in Chapter 12 [1–3]. This chapter provides an overview of building blocks for conventional polyurethane polymerization.

In principle, there is as much potential for design of isocyanate structures as there is for alcohol and amine coreactants. In reality, while there are numerous polyisocyanates to choose from, most of the innovation in polyurethane performance comes from the broad range of choices available in the coreactant alcohols and amines. To a great extent, this reflects complications (both industrial and regulatory) associated with making isocyanates and the comparative ease of making polyol and polyamine structures. It also reflects the fact that for most polyurethanes, nonisocyanate reactants comprise more than 50% of the polyurethane volume. Thus, for the purpose of obtaining any particular outcome, varying the polyol and the chain extender components is the most straightforward way to begin.

2.1 POLYOLS

The term polyol refers simply to polymer backbones containing nominally two or more hydroxyl groups. Polyols are the largest volume raw material used in polyurethane applications with weight fractions in applications ranging from 90 wt% in low modulus flexible sealants, 70 wt% in flexible foams, and as low as 30 wt% in rigid insulation foams. As implied by these values, the polyols in urethane formulations tend to provide softness and flexibility, while isocyanates and low-molecular-weight chain extenders provide hardness and stiffness to the resulting polymer structures.

Polyols are produced with a range of backbones and hydroxy functionalities that can be tailored to best meet application processing and property requirements. The most industrially significant polyol backbones are ether and ester based, while a number of specialty backbones including carbonate, acrylic, and ethers derived from tetrahydrofuran (THF) are used in high-performance coating, adhesive, and elastomer applications. Figure 2.1 shows their relative global volumes as of 2011 [4, 5]. For comparison, the relative global volume for polyether polyols in 1992 was 2654 thousand metric tons and for PTMEG was 100,000 metric tons [4]. In the case of polyether polyols, this translates to roughly 4% annual growth rate. The volume growth of PTMEG has also been a long-term trend of approximately 4% [6]. Despite continuity of the long-term trend, the growth in these categories has not been linear over time and not uniform over all geographies. For instance, it is estimated that while the current growth rate for polyether polyols in China is nearly 8%, it is only about 2.5% in North America. While the polyol industry as a whole has grown, the relative size of each category reflects the integrated underlying dependence on global economic growth in various regions.

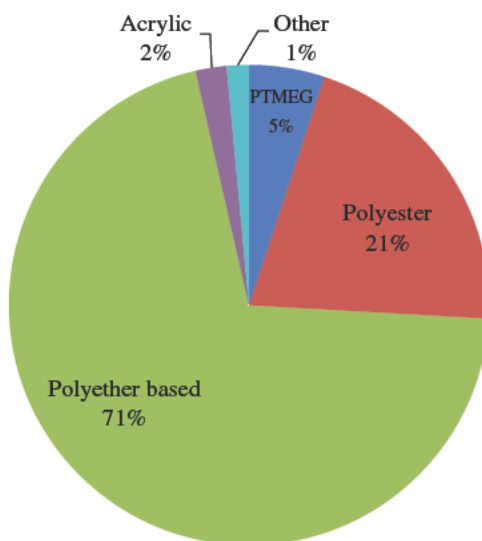


FIGURE 2.1 Relative volumes of polyols produced in 2011.

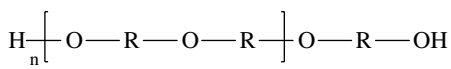
Polyols vary markedly in structure, manufacture, function, and price. While each occupies a particular price/performance niche, for many of them, there is an overlap, and the choice of which polyol to use in any particular application depends on the history and experience of the chemist and the end user. In general, polyols all begin with low-cost commoditized building blocks. Final cost depends on factors related to volume of production, cost of polymerization process, and perceived value in an application. The structures of several commonly utilized polyols are provided in Figure 2.2. The structure to a great extent defines the properties of the resulting polyurethane, as well as the compromises each structure demands of the final product performance. For instance, while polyethers generally provide good low temperature performance, an easily processed backbone, and a good cost position, the low ceiling temperature (the temperature at which the rate of depolymerization is equal to the rate of polymerization) is relatively low for these structures [7]. While many factors may influence the exact degradation temperature, these polyether polyols should not be considered stable above 220 °C. Polyether polyol flammability results from the high volatility of the monomers and the combination of oxygen and hydrocarbon fuel that the monomer represents and is a fundamental limitation to these structures [8, 9]. This problem has in turn created a demand for flame retardants in many polyether containing systems, especially foam systems having high surface to volume ratios [10]. Similarly, the well-known hydrolytic instability of polyesters is a compromise that must be accommodated if taking advantage of their low cost (in some instances) and high thermal stability (Table 2.1).

2.1.1 Polyether Polyols

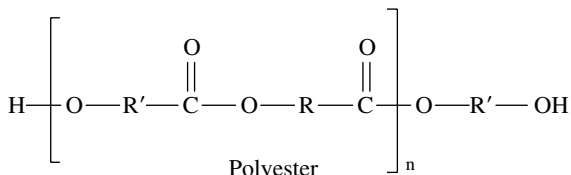
2.1.1.1 Building Blocks Polyether polyols are the class of polymers formed from the exothermic reaction of ethylene oxide (oxirane), 1,2-propylene oxide (methyloxirane), or 1,2-butylen oxide (ethyloxirane). Other materials could be considered (i.e., epichlorohydrin), but these monomers are the largest volume of this class and of the most use in polyurethane chemistry. Additionally, the related cyclic ether THF is another important building block for polyether synthesis (Fig. 2.3). Although the molecules are structurally related, each one is prepared by significantly different procedures.

Ethylene oxide is prepared directly from the catalyzed oxidation of ethylene [11, 12]. 1,2-Propylene oxide and 1,2-butylen oxide are prepared from a 2-step reaction consisting of reaction of the 1,2-alkene with chlorine and water to form the chlorohydrin followed by ring closure to form the cyclic ether by reaction with base [13, 14]. Figure 2.4 is an illustration of the synthesis of 1,2-butylen oxide.

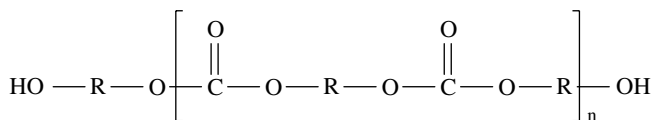
A more recent innovation produces propylene oxide (PO) by direct oxidation of propylene using hydrogen peroxide (HPPO process) [15, 16] (Fig. 2.5). The HPPO process is simpler and less energy consuming but requires the coproduction of hydrogen peroxide on a massive scale to make PO economically. A third industrial route to propylene oxide involves peroxidation of ethyl benzene to form ethyl benzene hydroperoxide followed by reaction with propylene to produce the desired propylene oxide and the side product methyl phenyl carbitol, which can



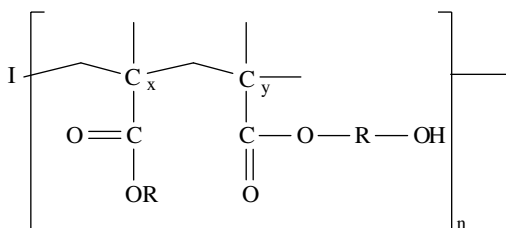
Polyether



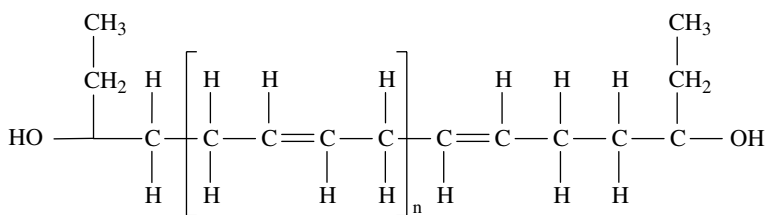
Polyester



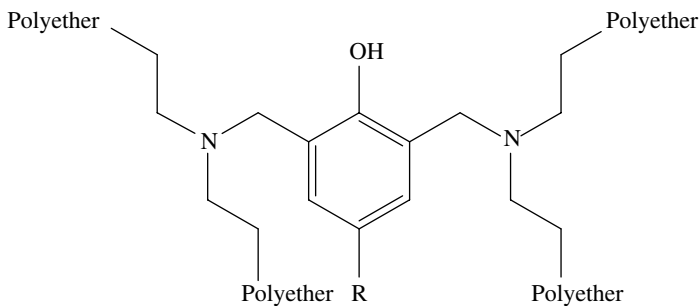
Polycarbonate



Acrylic



Polybutadiene diol

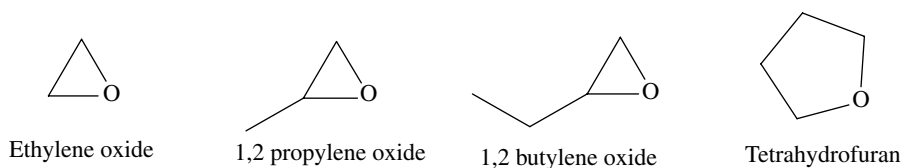
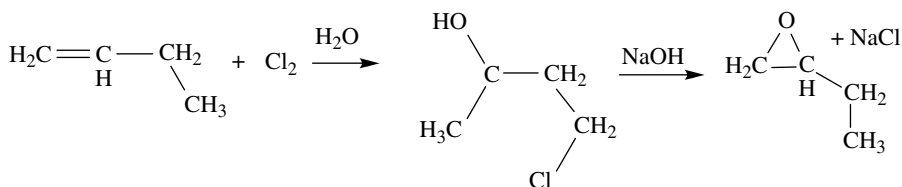
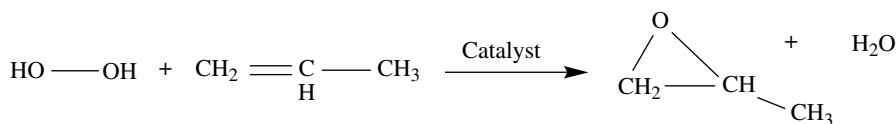


Mannich polyol

FIGURE 2.2 Comparison of basic polyol structures.

TABLE 2.1 Comparison of polyol general properties

Polyol backbone	Advantages	Disadvantages
Polyether polyols based on propylene oxide and ethylene oxide	Hydrolytic stability, cost, viscosity, flexibility	Oxidative stability, modulus/strength, thermal instability, flammability
Aliphatic polyester polyol	Oxidative stability, modulus/strength	Viscosity, hydrolytic stability
Aromatic polyester polyol	Flame retardance, modulus/stiffness	Viscosity, low flexibility
Polyether polyols based on tetrahydrofuran	Hydrolytic stability, modulus/strength	Oxidative stability, viscosity, cost
Polycarbonate polyols	Hydrolytic stability, oxidative stability, modulus/strength	Viscosity, cost
Acrylic polyols	Hydrolytic/oxidative stability, hardness	Viscosity, cost, low flexibility
Polybutadiene polyol	Low temperature flexibility, solvent resistance	Viscosity, thermal oxidizable (unless hydrogenated), cost

**FIGURE 2.3** Building blocks for polyether polyol synthesis.**FIGURE 2.4** Synthesis of butylene oxide via chlorohydrin route.**FIGURE 2.5** Synthesis of propylene oxide via hydrogen peroxide (HPPO) process.

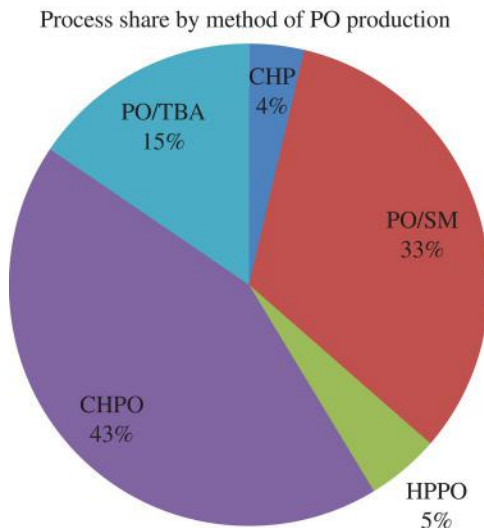


FIGURE 2.6 Volume of PO produced by the numerous routes available. CHP, PO by peroxidation using cumenehydroperoxide; CHPO, chlorohydrins process; HPPO, PO by peroxidation of propylene with hydrogen peroxide; PO/SM, PO co-styrene monomer; PO/TBA, PO co tert-Butyl alcohol.

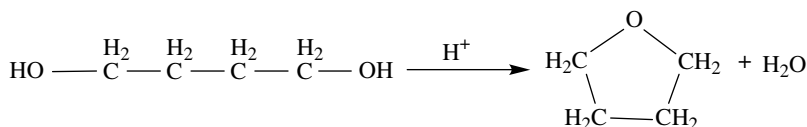


FIGURE 2.7 Production of THF via dehydration of butanediol.

be dehydrated to styrene [17]. Other methods also are practiced commercially [18]. Figure 2.6 details the share of each process to PO as of 2008.

The last feedstock for polyether production is THF. The great majority of THF is produced by dehydration of 1,4-butanediol [19]. Two alternative processes are practiced industrially. One route oxidizes butane to maleic anhydride followed by hydrogenation of the anhydride to THF [20]. A second route reacts butadiene with acetic acid and oxygen to form 1,4-diacetoxy butane, which can be hydrolyzed to 1,4-butanediol or THF by deacetoxy cyclization [21, 22]. While this route has the benefit of flexibly producing either the diol or the furan product, it creates increased demand for the valuable butadiene monomer with implications for those products requiring synthetic rubber. A new process produces THF from biosourced sugars by separation of succinic acid from the bacterial broth and reduction to butanediol and THF from the dehydration of butanediol [23] (Fig. 2.7).

2.1.1.2 Polymerization of Alkoxides to Polyethers While ethylene oxide is an important building block for synthesis of polyurethane polyether soft segments, there are only a few exceptions where polyethylene glycol (PEG) is utilized as the sole soft

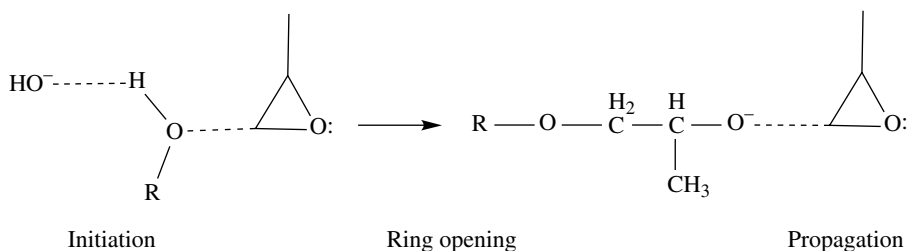


FIGURE 2.8 Production of polypropylene oxide via base catalyzed ring opening polymerization.

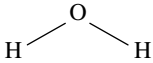
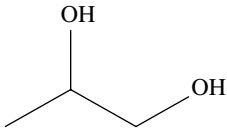
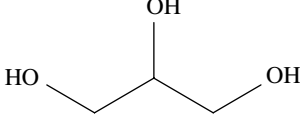
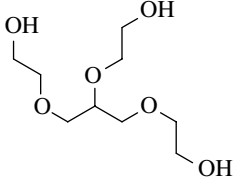
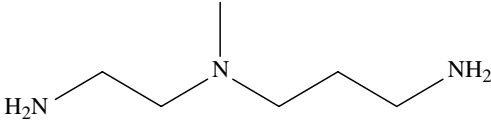
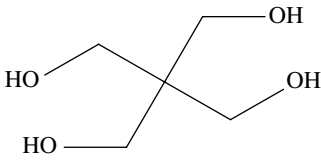
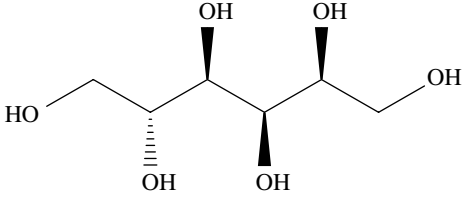
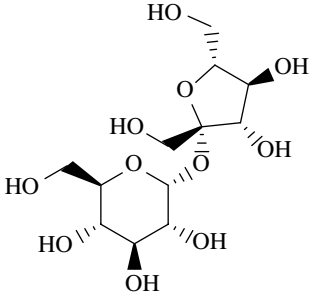
segment. This is because of the crystallinity of PEG and because of its affinity for water. The affinity for water limits PEGs use since the properties of the polyurethane can be strongly dependent on the humidity of the environment. Instead, for polyurethanes, ethylene oxide is usually used as a coreactant with other alkylene oxides, usually propylene oxides, to create block or random copolymers.

Propylene oxide is polymerized to polypropylene oxide by two industrially dominant processes. Both processes are defined by the catalyst that is used. The dominant method employs an initiator or starter molecule with active hydrogens such as water, ethylene glycol, glycerine, ethylene diamine, or sorbitol and a base catalyst like potassium hydroxide [24]. This approach is usually referred to as the base-catalyzed process. The other process to polypropylene oxide uses a class of heterogeneous metal-based catalysts termed “double-metal cyanide” catalysts (aka DMC catalysts) [25]. Each process has unique attributes including differences in cost, process flexibility, and even structure of the final product. The base-catalyzed process follows the simplified path given in Figure 2.8.

The functionality of the final product is determined by the functionality of the initiating alcohol (see Table 2.2) and the final molecular weight influenced by the ratio of initiating alcohol to oxirane monomer. The base resides in a molecularly dispersed state with the oxirane and is termed a homogeneous catalyst. In actuality, the process is more complicated than expressed in Figure 2.8. The reaction mechanism of Figure 2.8 suggests that the result of the reaction is all secondary hydroxyl end groups. However, this is not in fact observed. In the synthesis of polypropylene oxide, there are also observed a population of primary hydroxyl end groups and a population with vinyl termination. The vinyl termination is a particular concern since it is not reactive with the other components of polyurethane chemistry and so degrades the polymer network structure. The actual chemistry that occurs within the reactor is explicitly given in Figure 2.9. The reaction resulting in secondary hydroxyls predominates, but the other structures do form and the process and specific product influence the product distribution.

The primary product in base-catalyzed (or explicit in these reactions—*base initiated*) polymerization is the product predominated by secondary hydroxyls due to the relative ease of nucleophilic attack on the less hindered carbon of the oxirane. Alkoxide attack on any of the methyl hydrogens results in unsaturation given

TABLE 2.2 Common polymerization starters or initiators for polyether polymerization

Initiator	Initiator functionality	Structure
2	Water	
2	Ethylene glycol	
2	1,2-Propylene glycol	
3	Glycerine	
3	Ethoxylated glycerin	
4	Ethylene diamine	
4	<i>N</i> -methyl-amino-dipropylamine	
4	Pentaerythritol	
6	Sorbitol	
8	Sucrose	

mechanistically in Figure 2.10 for the formation of allyl alcohol, which can then serve as the initiating alcohol for monohydroxy polyether formation referred to as “monol” [26].

The amount of monol formed in the polymerization is a function of several process details increasing primarily with temperature. An empirical equation for estimation of polyol functionality taking into account the effect of monol is given by Equation 2.1 [27]:

$$\text{Functionality} = \frac{\% \text{OH} / 1.7}{\text{unsat} + \frac{\left(\frac{\% \text{OH}}{1.7} \right) - \text{unsat}}{\text{nominal functionality} - \text{mole\% diol}}} \quad (2.1)$$

Alternatively, the functionality can be calculated from the measured OH number (ASTM D4274) [28] and the ASTM measured allyl concentration using Equation 2.2:

$$\text{Functionality} = \frac{\text{OH}/56.1}{((\text{OH}/56.1) - \text{unsat}) \times (1/\text{nominal functionality}) + \text{unsat}} \quad (2.2)$$

The amount of unsaturation is measured by a standard method such as ASTM D4671 [29]. Unsaturation is quantified in units of “milliequivalents unsaturation per gram of polyol,” and the diol content is obtained from either chemical analysis or by calculation. Figure 2.11 shows the potential loss of network connectivity resulting from formation of unsaturation of a nominally 5000 molecular weight triol. Similarly, a 4000 molecular weight diol can have a true functionality of 1.7 due to monol formation.

Ethylene oxide cannot form unsaturation in the manner of propylene oxide since there is no beta carbon from which to abstract a hydrogen. Butylene oxide is capable of forming an unsaturated monol initiator in a manner analogous to propylene oxide.

The problems associated with monol formation have stimulated research for alternative polymerization catalysts less prone to formation of unsaturation. One approach has been to vary the complexing counterion. It has been shown that the tendency for the counterion to promote formation of allyl alcohol decreases in order down the periodic table from $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$. It has been reported that the use of CsOH instead of KOH can reduce the formation of unsaturated end groups by 50% [30, 31]. Alkaline earth salts bearing Ba^{+2} and Sr^{+2} have also been reported to result in significantly reduced formation of unsaturation in polyether synthesis [32].

As with all homogeneous catalysts, the base must either be extracted or neutralized after the polymerization step. If the polyol is sufficiently immiscible with water, the catalyst can be extracted with water. The polyol will coalesce as a separate phase and be easily removed and, if necessary, the catalyst recovered. In general, the rate of base-catalyzed reaction is considered to be first order in catalyst and in oxirane:

$$\text{Rate} = K_2 [\text{oxirane}] [\text{catalyst}] \quad (2.3)$$

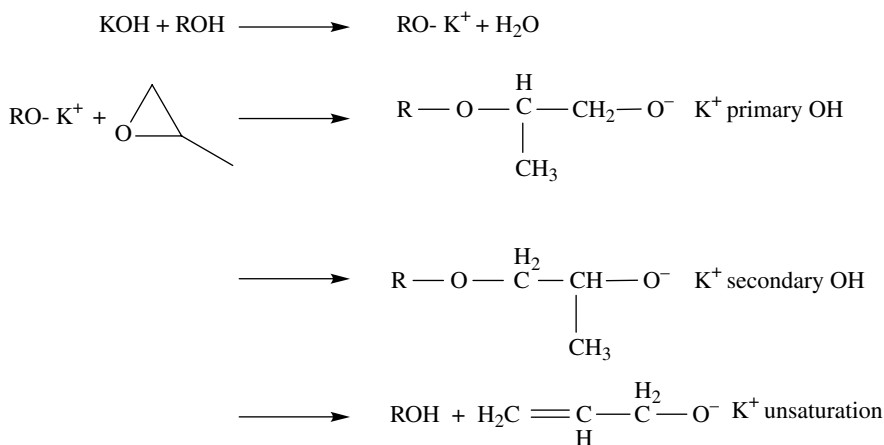


FIGURE 2.9 Possible pathways PO polymerization can traverse to products. The route to secondary hydroxyls is the most prevalent.

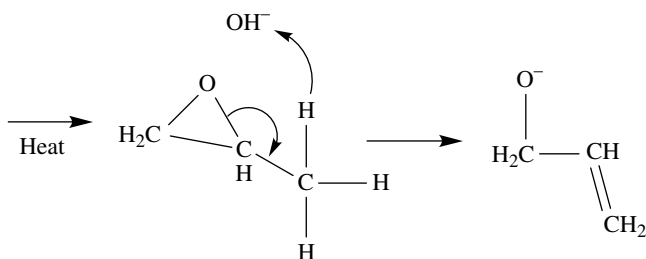


FIGURE 2.10 Mechanism for formation of unsaturation in polyether polyols. PEGs cannot do this due to the absence of pendant carbons for attack.

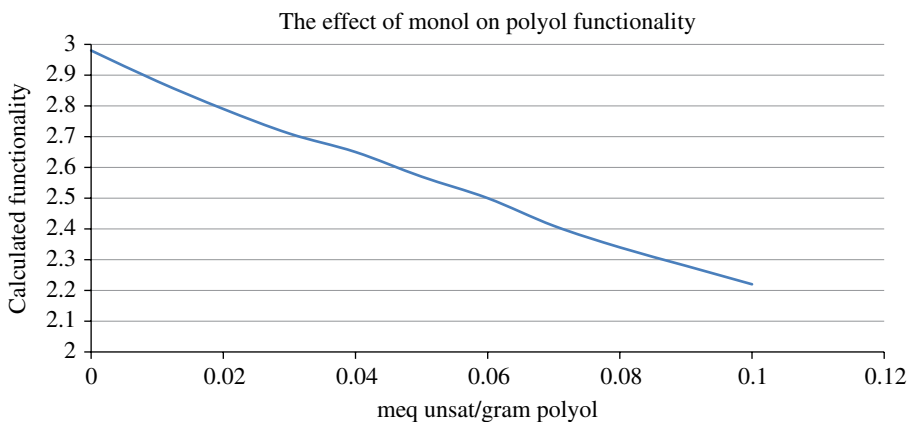


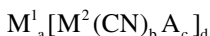
FIGURE 2.11 The calculated actual functionality for a for a 5000 molecular weight (1666 equivalent weight) triol reflecting the effects of end-group unsaturation developed during polymerization.

where K_2 is the second-order rate constant. However, since the catalyst is not consumed, the rate can be further simplified to Equation 2.4:

$$\text{Rate} = K_1[\text{oxirane}] \quad (2.4)$$

where K_1 is a pseudo first-order rate constant equaling the product of $[\text{catalyst}] \times K_2$.

Separate from the homogeneous base initiation of oxirane polymerization, a heterogeneous catalyst system has been developed. The most successful approach has been the development of heterogeneous catalysts described collectively as “DMC” catalysts [33]. DMC describes any of the class of catalysts of general structure



where M refers to a metal, CN refers to the CN ligand, and A is an additive.

The effectiveness of DMC catalysis in polymerization of epoxies was first noticed in the early 1960s and rediscovered for the purpose of polypropylene oxide production by Shell, Arco, Asahi Glass, Union Carbide, and others in the 1980s. Considering the amount of time and effort that has been put into this very enticing class of catalysts, it remains safe to say that there are many open questions about how they operate. While DMC catalysts show a high level of reproducibility and reliability in their function, this technology has largely advanced through empirical observation and what can only be termed as “art.”

The most efficient DMC catalysts for polymerization of polypropylene oxide contains $Zn_3[Co(CN)_6]_2$ scaffolding in its structure. However, it is well established that this structure alone is inactive for polymerization of propylene oxide and that additional additives must be incorporated for desired results. DMC additives typically include metal salts such as $Zn(Cl)_2$ and low-molecular-weight solvents such as tert-butanol [34]. Preparation of the optimized active catalyst is an involved and precise procedure. The mechanism of the catalyst is highly uncertain. The catalyst is sometimes referred to as a “precatalyst” since there is usually an induction time on the order of 30 min to several hours between when reaction conditions are reached and when molecular weight build due to polymerization commences. Several theories exist for this behavior; however, given the fundamental limitations of precisely determining the surface conditions during reaction, full understanding remains an area open for research.

One mechanism suggested for the action of DMC catalysts involves the initial substitution of the Cl ligand of $ZnCl_2$ with the alcohol (i.e., tert-butanol) stated in the previous text to be necessary for catalyst activity [35]. Another substitution of Cl on the Zn metal center coordinates the reactive species to a single site in a geometry potentially effective for an addition reaction to occur. Proton transfer from the alcohol coordination site to the Zn-PO bond ring opening would be facilitated. This model is consistent with the observation that too much alcohol ($R'OH$ in Fig. 2.12) depresses the activity of the catalyst. In this scheme, too much $R'OH$ would possibly compete with the alkoxide for coordination to Zn [36]. It is not immediately clear how this model accounts for the induction period, though it is possible to rationalize that

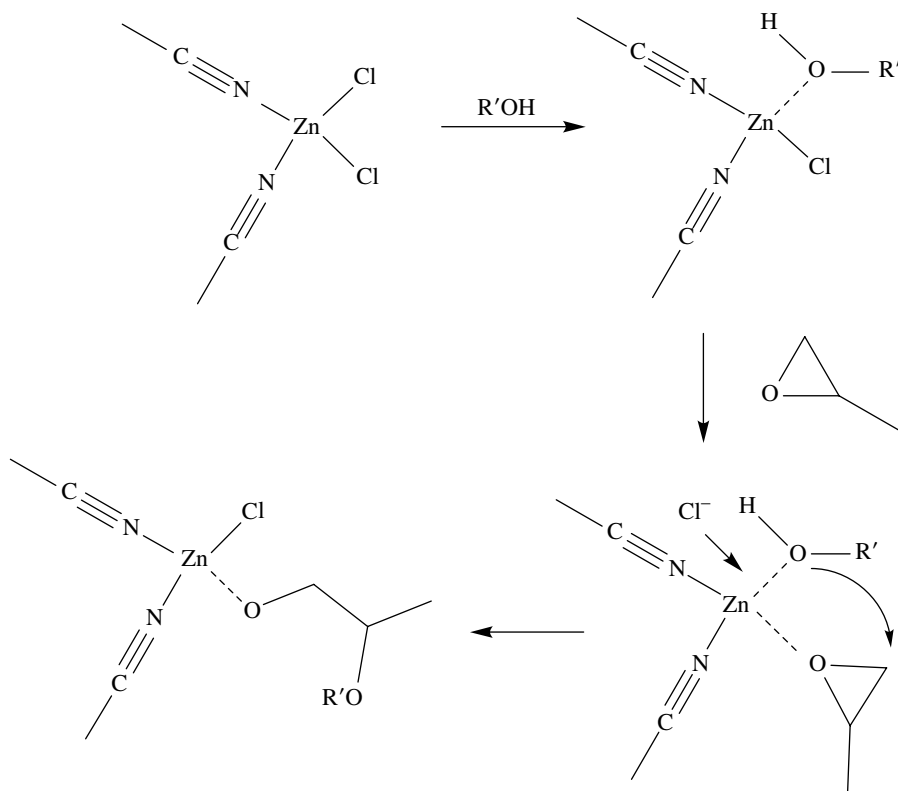
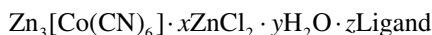


FIGURE 2.12 Proposed coordination-insertion mechanism for activity of DMC catalysts polymerizing propylene oxide.

attaining the condition of cocomordinate alcohol *and* alkoxide may take time and may depend on such experimental details as mixing, temperature, the population of active catalyst sites on the surface, etc. Similarly, it is not immediately clear why the ratio of Zn to Co in the catalyst package has such a significant effect on catalyst activity.

An alternative (but somewhat related) mechanism also relies on coordination of reactants to the surface but takes into account the totality of the catalyst morphology including its layered structure and the coordination geometry. As mentioned previously, when the entire catalyst package including added metal salts such as ZnCl_2 is taken into account, the total formula for the catalyst can be generalized from $\text{Zn}_3[\text{Co}(\text{CN})_6]_2$ to



For a Zn/Co ratio of 1.5, each Zn is coordinated to four cyanides and lacks a coordination site (assuming 4-coordinate Zn). In fact, it is established that DMC catalyst activity for this series of catalysts requires a Zn/Co ratio greater than 1.5. For a Zn/Co of 2.0, zinc obtains a population of coordination conditions with an average

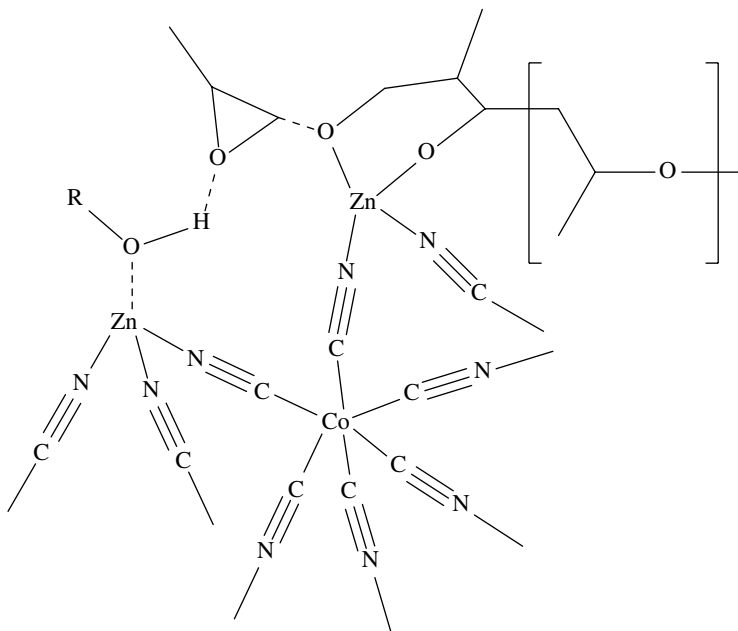


FIGURE 2.13 Proposed acid-base coordination mechanism for activity of DMC catalysts polymerizing polypropylene oxide.

of three cyanides and one chloride for every two zinc ions. By this model, a surface fragment of DMC catalyst may have two Zn sites: one acid capable of binding to an alcohol function and, the other, a basic site capable of binding to an alkoxide. The binding of the alcohol to the acid can activate the proton as suggested in the model described by Figure 2.12. Figure 2.13 describes this model for the acid–base-regulated coordination chemistry.

Regardless of the details of the mechanism of DMC polymerization of polyols, there are several advantages associated with this process. These include higher activity at any given temperature (allowing low catalyst loadings), narrow molecular weight distributions, a highly atactic product (low tendency to crystallize), and very low levels of unsaturation, well under 0.01 meq/g (see Fig. 2.14 for comparison to KOH). The meaning of the lower unsaturation to the polymer structure can be seen in Figure 2.14. Since the number of end groups decreases rapidly with increasing molecular weight, and the formation of unsaturation is dependent on reaction conditions but are otherwise fixed, the effects of unsaturation on polyurethane network connectivity will intensify as the molecular weight increases. The differences between KOH- and DMC-catalyzed polymerizations become more noticeable at equivalent weights greater than 1000 g/eq [37].

The obvious advantages associated with DMC catalysis in the final product come with a price. A well-known process caution is associated with the induction period. Given the very high activity of DMC-catalyzed ring opening and the high

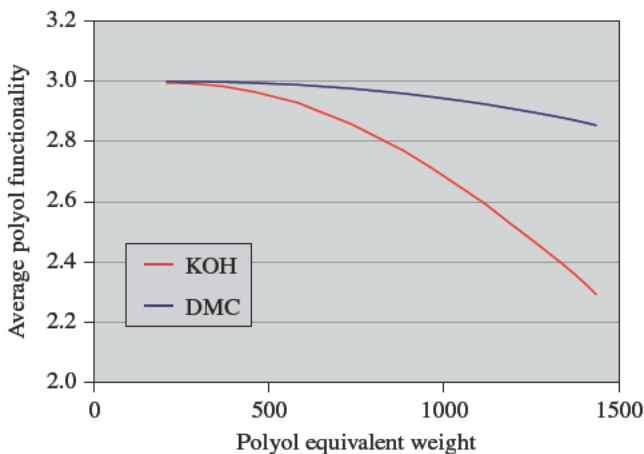


FIGURE 2.14 Difference of measured polyol functionality attained by KOH and DMC catalysis for a triol of variable equivalent weight. The difference becomes appreciable at higher equivalent weights as the number of end-groups decreases. Reprinted with permission from Ref. [37]. © John Wiley & Sons, Inc. (See insert for color representation of the figure.)

exotherm of the reaction (~ 25 kcal/mol), the induction results in a very significant and potentially unpredictable exotherm produced during the polymerization. Process optimization has dealt with this on an industrial scale by standardization of materials and process [38].

A larger and more intractable problem is the inability to develop block copolymer structures of ethylene and propylene oxide. As will be discussed later, there is a significant reactivity difference between the secondary hydroxyls from polypropylene oxide and the primary hydroxyls of polyethylene oxide. One processing compromise to obtain primary hydroxyls without the drawbacks of all PEG structures is to polymerize PO to polypropylene oxide to a given molecular weight and subsequently add EO. When handled appropriately, homopolymerization of the EO can be minimized, and ethylene oxide blocks can grow from the PPO polymer ends. With KOH catalysis, this is not a problem since PO and EO can be equally polymerized via the mechanism of Figure 2.9. A similar process has not been achieved with DMC catalysis. The reason for this has not been well established. One hypothesis has been that the growing PEG block has a much higher affinity for the DMC catalyst surface causing the initially formed end blocks to grow inhomogeneously. The ever-growing PEG blocks become ever less miscible with the PPO bulk, and so polymer chain exchange off the surface to the bulk becomes increasingly less favorable. Instead, obtaining EO-capped PPO polyols prepared by DMC catalysis has required deactivation of the DMC catalyst followed by EO end capping using conventional KOH catalysis. A process in which EO mixed with the PO in the reacting mixture has been developed and proven effective at producing random PO/EO polymer chains [39].

A product-related problem with DMC catalysis is ironically caused by the high level of patent activity that has been pursued by a few competitors. The result has

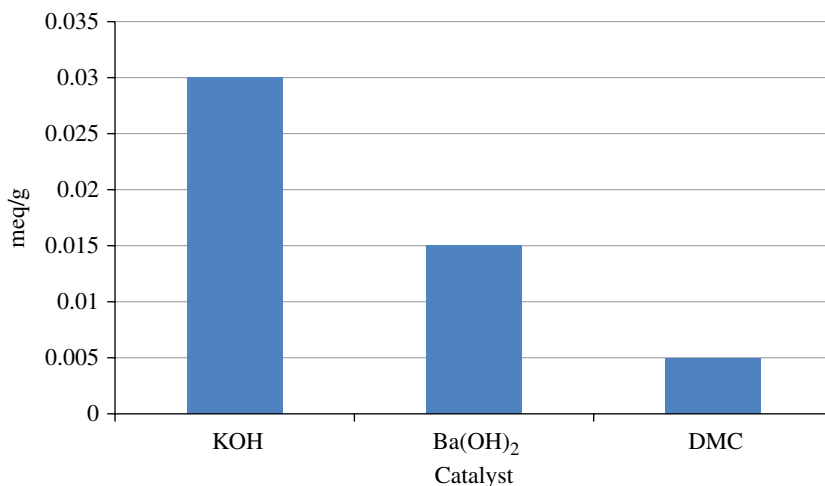


FIGURE 2.15 Measured unsaturation levels by titration of three polyols for a 2000 molecular weight diol. The lower the value the less vinyl end groups found in the system [40].

been that only a few industrial concerns have developed or licensed patent coverage for making DMC-derived polyols. At the same time, there have been advances in traditional base catalysis using varied counterions (Fig. 2.15). The motive for further innovation in heterogeneous coordination catalysis has also been dampened by the observation that polyurethane foam properties, accounting for a large volume of polyurethane usage, are not noticeably affected by the undeniable polyol structural improvements derived by DMC catalysis. This has relegated DMC polyols to nonfoam applications—those applications where the low reactivity of secondary hydroxyls is irrelevant. DMC-catalyzed polyols are also preferred for higher equivalent weight polyols since at lower equivalent weights the structural differences are minimized as the fixed number of vinyl chain ends is less important due to the large number of total chain ends.

Today, the vast majority of industrially produced polyols are prepared by KOH-catalyzed polymerization of PO or PO/EO monomers. The process in concept is remarkably simple, but the details associated with producing a commoditized product can create significant amounts of redundancy, controls, and safety additions. To make polyols efficiently and competitively, the production volumes must be very large and the accompanying costs very large as well. Plant capacities range from about 50 thousand metric tons to about 500 thousand metric tons. For the purpose of scale, a 50 thousand metric tons/year plant can produce about 12 thousand lbs/h of polyol. Smaller quantities are sometimes produced by enterprises that use the entirety of their product captively. Figure 2.16 provides a very simplified view of a polyol plant process to nominally produce a three-functional (vis-à-vis glycerin) 12.5% ethylene oxide-capped PO or a random PO/EO polyether polyol by a batch process [40]. Also provided are the approximate unit ratios required to make that polyol 1000 g/OH eq. An important and unappreciated component of the process is the

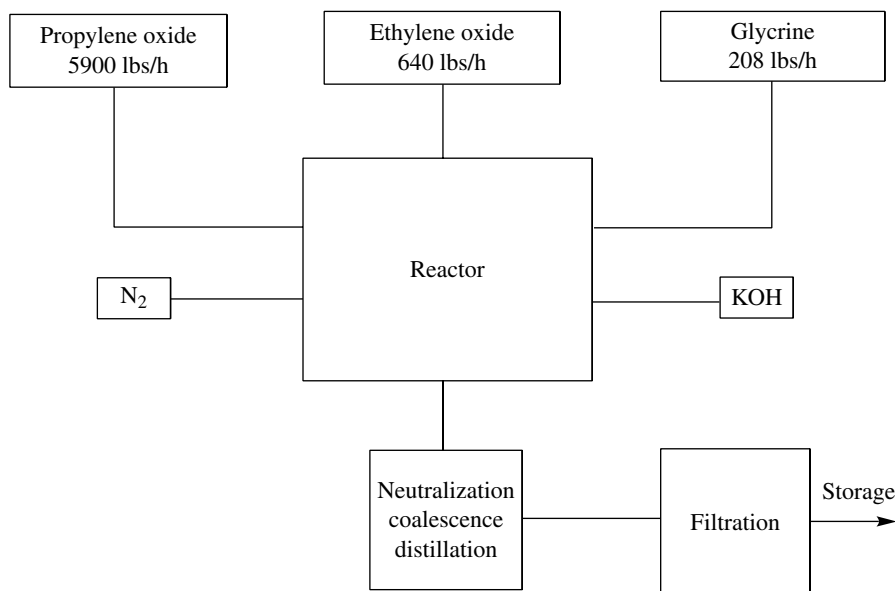


FIGURE 2.16 Simplified block diagram for a small polyol production of a glycerine initiated (triol) KOH catalyzed PO/EO block co-polymer (12.5% EO) with total molecular weight 3000 (equivalent weight 1000 g/eq).

treatment stage at which unreacted monomer may be driven off and the KOH removed by filtering with magnesium silicate, or neutralized with acidified water, and the polyol coalesced as a separate phase from the water and decanted. These neutralization and filtering steps are important aspects of the process and an important component of process research when introducing a new product.

The polyether polyols from THF (referred to commonly as *polytetramethylene ether glycol* (PTMEG)) are treated separately here and in many other places for several reasons. One reason is because, although a relatively high volume polymer (~500 million pounds/year) [41], PTMEG occupies a specialty position within polyurethane chemistry as a whole. As a specialty, it is produced at smaller volumes, by a significantly different process, and at much higher costs to manufacture and prices to the consumer. Growth rates are in-line with most other polyols (~4% per annum) reflecting growth in the overall global economy. The major uses by volume for PTMEG are polyurethane elastomers, sealants, adhesives, polyesters, and spandex fibers.

The production of PTMEG is achieved by two routes [42]. The most common way is via acid-catalyzed ring-opening polymerization (Fig. 2.17). This path has the advantages of simplicity. The most common acid is fluorosulfonic acid, although other variations are practiced as well. Disadvantages of this process include inability to recover the acid, the potential for the acid to degrade the product, and difficulties in molecular weight control due to the limited but still finite ability of terminal hydroxyl groups to be deprotonated and initiate polymerization.

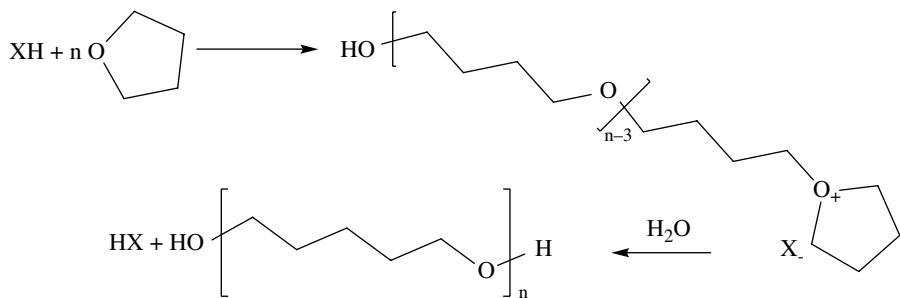


FIGURE 2.17 Acid catalyzed polymerization of THF to make polytetramethylene ether glycol (PTMEG).

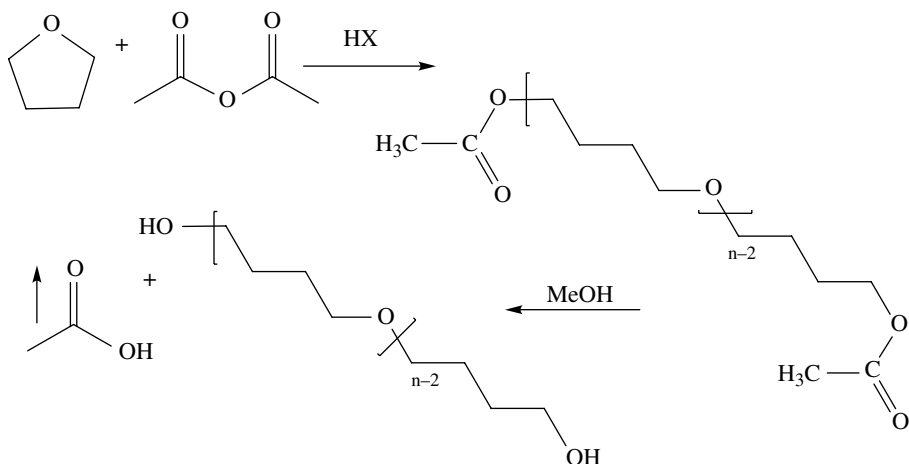


FIGURE 2.18 Process for preparation of PTMEG by reaction of THF with acetic anhydride to form the stable ester.

An alternative process has been established producing the final polyether product by preparation of an intermediate but stable diacetate ester, which can subsequently be converted to diol by alcoholysis (Fig. 2.18) [43]. The greater stability of the ester end group in this environment allows for better molecular weight control.

While many older plants utilize the acid-catalyzed polymerization route, there has been significant optimization of the acetic anhydride polymerization process now used by many newly constructed plants. Industrial production always entails separation of unwanted side products by either volatilization or filtration and recycling of unused reagents back to earlier stages of the reaction. Figure 2.19 is a highly simplified version of what would be included in a real plant but does provide detail of the primary unit operations.

Because of the similarity of polymerization processes, monomers of polyether polyols synthesis are very amenable to copolymer design. Virtually any imaginable

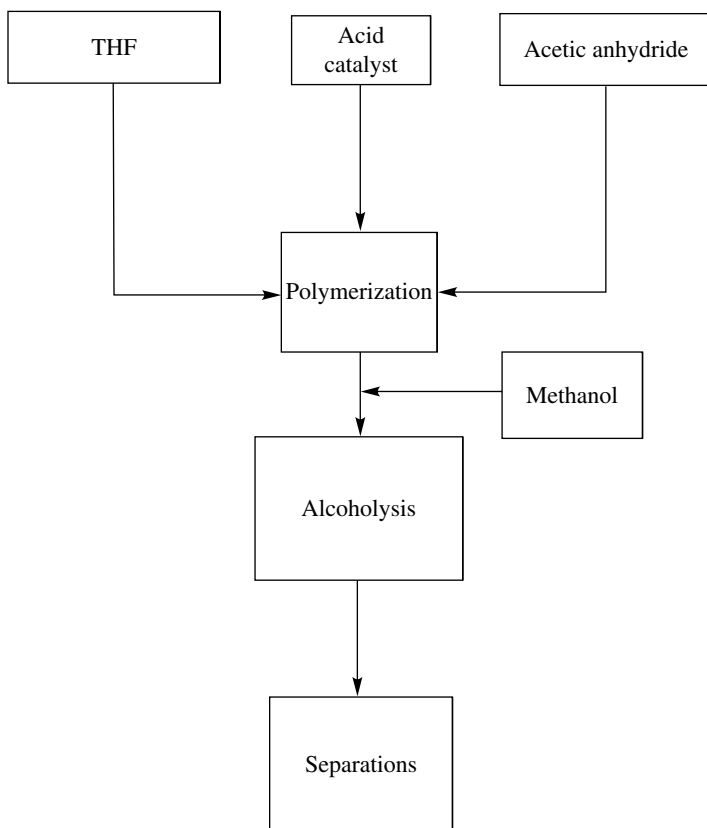


FIGURE 2.19 Simplified block diagram for production of PTMEG using acetic anhydride/alcoholysis process.

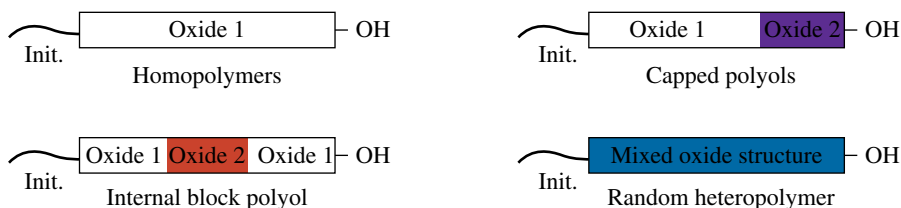


FIGURE 2.20 Cartoon representations of the types of co-monomer organization available to produce polyalkylene glycol soft segment structures. Reprinted with permission from Ref. [37]. © John Wiley & Sons, Inc.

design and combination of oxirane monomers have been combined to examine properties and look for advantageous structures. Figure 2.20 illustrates the various combinations that are imaginable with these building blocks.

The most common type of block copolymer structure is the internal block polyol in which a polypropylene oxide block is reacted at either end with ethylene oxide to

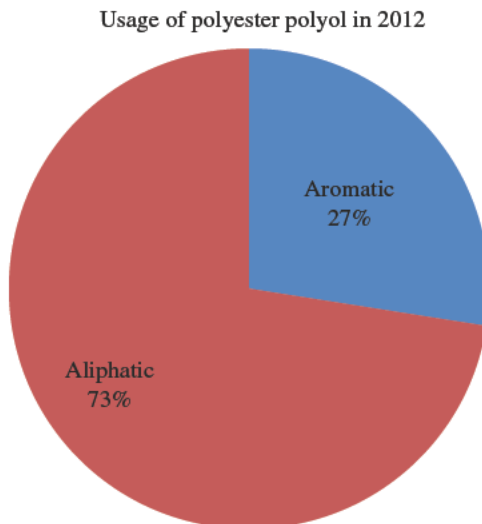


FIGURE 2.21 Fractional consumption of polyester polyols in 2012.

balance the low T_g , low tendency to crystallize with the relatively high reactivity of the primary hydroxyl end group.

2.1.2 Polyester Polyols

As shown in Figure 2.1, polyester polyol production is only about 25% of the total polyol production; however, given the scale of the industry and the importance and ubiquity of polyester polyols, the impression from the pie chart could be misleading. Indeed, the world capacity for polyester polyols in 2012 was about 2300 thousand metric tons and actual consumption at about 1900 thousand metric tons (~4.2 billion pounds!). The annual growth rate of polyester polyol consumption is about 4%, similar to polyether polyols, and approximately mirrors the growth of the world and local economies. Within polyurethane production, polyester polyols are a key feedstock in coatings, adhesives, elastomer, and rigid foam formulations. Depending on the application, an aromatic or an aliphatic diacid will be employed to deliver the desired suite of properties. As will be discussed in detail, aromatic polyesters are usually deployed for the purpose of enhancing flame retardance [44], increased T_g , and reduced gas permeability and so are widely used in polyurethane insulation foams. Aliphatic polyesters used in urethane formulations enhance tensile strength, abrasion resistance, UV resistance, and low temperature flexibility (low T_g) and find primary use in coatings and elastomers. Although the synthetic procedures for preparation of aromatic and polyester polyols are similar, the properties and applications are diverse enough to warrant their separate treatment.

Figure 2.21 breaks out the approximate differential consumption of aromatic and aliphatic polyester polyol consumption. The usage of aromatic versus polyester polyols is not uniform across geographies. Aromatic polyols are used to a much greater extent in the United States due to consumer expectations for superior flame

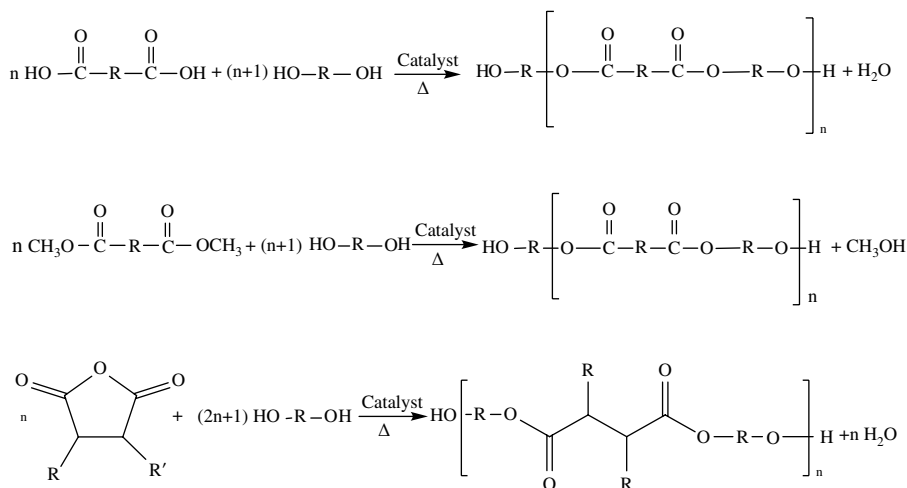


FIGURE 2.22 Polymerization of polyesters via esterification reaction between a dialcohol and a diacid, transesterification between a diester and a dialcohol and ring opening polymerization between an acid anhydride and a dialcohol.

retardance, structural integrity, and thermal insulation properties found in polyurethane and polyisocyanurate insulation panels [45]. The relative usage of aliphatic polyester polyols is much higher in China due to the relatively high manufacturing for coatings, elastomers, artificial leather, etc. [4].

2.1.2.1 Polyester Polyol Building Blocks Polyesters are a class of polymers allowing for an enormous amount of structural and property design. Polyesters are the products of condensation polymerization between polyhydroxy and polyacid monomers. In some cases, a polyester or anhydride monomer is substituted for the polyacid, usually dependent on processing parameters related to difficulties associated with insoluble acids, inconvenience associated with relative cost, methanol toxicity, or incompatibility of manufacturing materials with the condensation water product (Fig. 2.22). Polyester chemistry is relatively straightforward, the monomers are usually not expensive, and the polymer properties are reasonably easy to anticipate [46]. There are a large number of building blocks and a large number of commercial polyesters to choose from when designing a specific polyurethane. Table 2.3 is an abbreviated but representative list of common building blocks for construction of polyester soft segments for polyurethane synthesis.

Although the process of combining polyacids and polyalcohols to form polyesters is generically similar in every case, the individual monomers are obtained from vastly different building blocks and sources. In fact, each building block can be obtained by multiple routes, each one having advantages, disadvantages, and economic sensitivities. For instance, adipic acid can be obtained from cyclohexane or from butadiene [47]. Butanediol can be obtained from propanediol (to allyl alcohol followed by hydroformylation and hydrogenation), acetylene, and formaldehyde or from fermentation of

TABLE 2.3 Structures of acids and alcohols common to polyester polyol synthesis for making polyurethanes

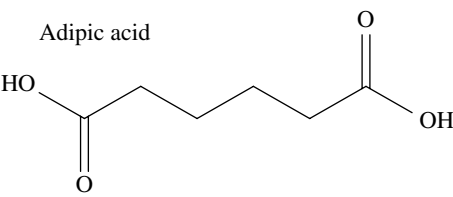
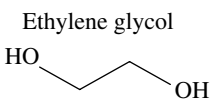
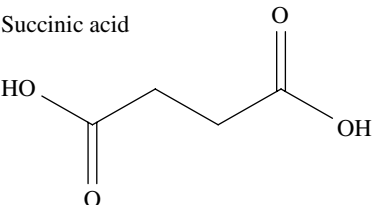
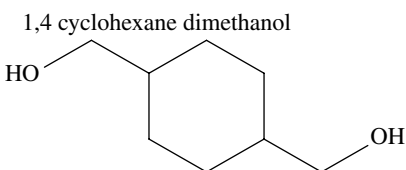
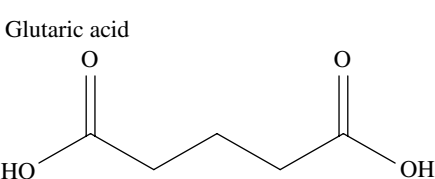
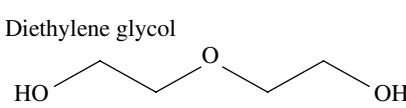
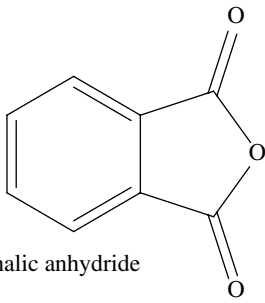
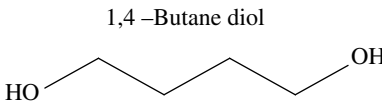
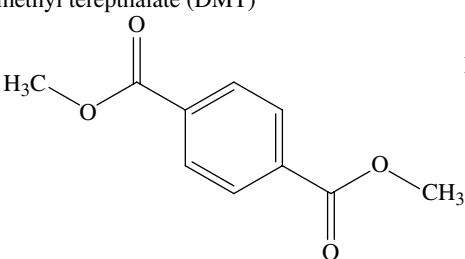
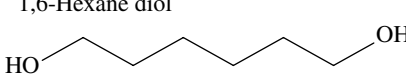
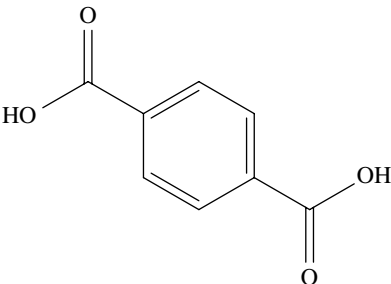
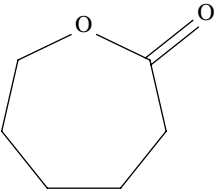
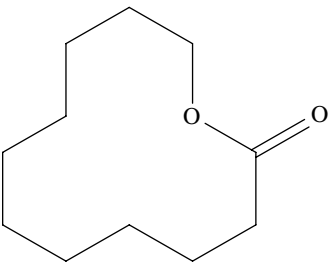
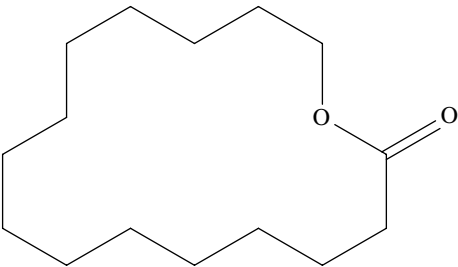
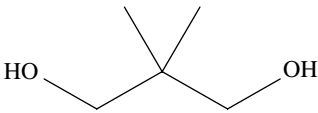
Examples of acids and anhydrides	Examples of glycols and diols
Adipic acid 	Ethylene glycol 
Succinic acid 	1,4 cyclohexane dimethanol 
Glutaric acid 	Diethylene glycol 
Phthalic anhydride 	1,4 -Butane diol 
Dimethyl terephthalate (DMT) 	1,6-Hexane diol 

TABLE 2.3 (Continued)

Examples of acids and anhydrides	Examples of glycols and diols
Terephthalic acid  Caprolactone  Undecalactone  Pentadecalactone 	Neopentyl Glycol 

sugar to succinic acid followed by reduction [48]. Terephthalic acid is produced by oxidation of xylene [47]. Thus, each of these monomers will vary in price independently of all the others, their manufacturers will be independent of one another, and the macro-economic pressures may vary independently. In contrast to polyether manufacturers who generally are back integrated into the building blocks (EO, PO, THF), polyester polyol manufacturers purchase building blocks such as those in Table 2.3 from several sources and will qualify multiple sources as primary suppliers using contracts and futures strategies. This also results in polyester manufacturers being “middleman” manufacturers, primarily suppliers to other businesses. Thus, the three largest polyester manufacturers in the world are, in order, Stepan Corporation, Coim Corporation, and Huafeng Group, all certainly well-regarded companies, but not generally well known or in the popular consciousness. The lone exception in this regard would be BASF, which is a major chemical manufacturer with extensive back integration into polyester building blocks and forward integration into products that use polyester polyols. On the other hand, BASF produces only about 1/2 the volume of either of the two largest polyester polyol producers [45].

2.1.2.2 Preparation of Polyester Polyols The desired product of polyester polyol synthesis is a polyester with high levels of terminal hydroxyl functionality. Achieving this goal is facilitated by applying the Carothers equation for determining the ratio of acidic and alcoholic monomers to get the desired molecular weight and hydroxyl functionality [49, 50]. In preparation of a simple linear polyester, this would take the form of

$$\frac{\text{Moles diol}}{\text{Moles diacid}} = 1 + \frac{1}{n} \quad (2.5)$$

where n is determined by considering one unit of diol as a chain initiator and the monomer unit to be the condensation unit of (diacid + diol – 2H₂O). Thus, the target Mn is calculated as

$$M_n = MW_{\text{diol}} + n \cdot MW_{\text{monomer}} \quad (2.6)$$

As an example, if the desired result is a 2000 molecular weight polyester polyol of polybutylene succinate, the MW_{monomer} is

$$118 (MW_{\text{succinic acid}}) + 90 (MW_{\text{BDO}}) - 36 (2 \times MW_{\text{H}_2\text{O}}) = 172 \quad (2.7)$$

$n = \text{moles monomer} / \text{moles initiator} = \text{moles adipic acid} / (\text{moles BDO} - \text{moles adipic acid})$ and a molar ratio of diol to diacid of 1.09. In practice, this result should be used as a theoretical guide and not as strictly predictive. The final result will reflect details of the polymerization procedure and systematic errors resulting in loss or decomposition of monomer or polymer over time. Nuclear magnetic resonance and chromatography are commonly applied to determine molecular weight, and titration of acid end groups by well-known techniques is applied to determine the level of hydroxyl functionality.

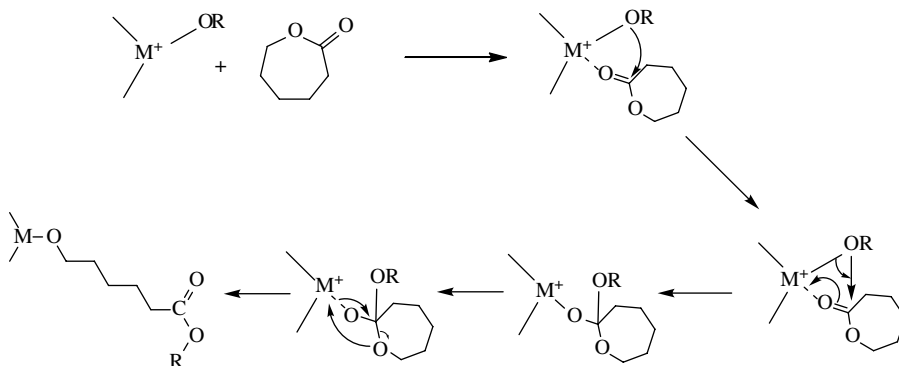


FIGURE 2.23 Accepted mechanism for coordination-insertion ring opening polymerization of ϵ -caprolactone to polycaprolactone.

Polyester polymerization can often be done without the need of a solvent since many of the monomers melt and phase mix prior to reaction. Polyester formation involves formation of a condensation product (for instance, water when using a diacid, methanol when employing a dimethyl ester) and the polyester products are in equilibrium with the reactants [51]. For this reason, condensation water (for instance) must be removed as the ester is formed, or high-molecular-weight polymers cannot be formed. This is usually achieved by sweeping a nonreactive gas such as N_2 over the polymer surface. As polymer forms, the molecular weight increases and the viscosity of the melt increases—linearly at first and to the 3.4 power above the entanglement molecular weight. The increase in melt viscosity can interfere with removal of the condensation product and slow the reaction down markedly. There is a temptation to increase the melt temperature to reduce viscosity, which in principle will facilitate removal of the water or alcohol. But increasing temperature may also facilitate the differential evaporation of the monomers. This will upset the calculation of monomer ratios required to obtain a specific molecular weight with terminal hydroxyl functionality and result in a stubborn lack of molecular weight advancement or sudden increases in molecular weight and the number of acid terminal groups far above that expected based on calculation. Such occurrences, as often occur in the laboratory in the absence of well-established procedures, will initiate the addition of diacid or diol in order to adjust molecular weight and/or reduce the prevalence of acid end groups.

The production of polyester polyols by ring-opening polymerization of lactones has also been explored extensively and many synthetic procedures and catalyst alternatives have been developed. One of the most common approaches employs a small polyol initiator (diol or higher) as an initiator and propagates chain extension through a coordination–insertion mechanism (Fig. 2.23) [52, 53]. The catalyst of choice for this approach is usually a tin or titanium alkoxide or other common catalyst used for polyester polymerization. The case where R is a polyol results in a polymer with three polymer arms and can be used to control the final molecular weight of the product.

2.1.2.3 Aliphatic Polyester Polyols Many aliphatic polyester polyols have been prepared and at one time or another been offered on the market. Despite this, and by far, the largest volume aliphatic polyester polyol used in polyurethane applications is polybutylene adipate followed by polycaprolactone. The ratio of polybutylene adipate to polycaprolactone production is approximately 100:1 [45]. The properties of the polyester polyol are of course a function of the diacid and diol building blocks used to produce the polymer. The properties of the polyester polyol are most easily accessed by their thermal properties. Table 2.4 provides a limited view of the thermal properties based on the polyester components.

A simple analysis of trends in the polylactone sequence shows that the carbon length between ester linkages is strongly influential on the crystalline melting point and the crystalline melt enthalpy, asymptotically approaching that of polyethylene (Fig. 2.24). For polyesters prepared from diacids and diols, a simple analysis of crystalline melting point and enthalpy shows virtually no correlation relative to the length of the diol, with a square of the correlation coefficient ($r^2=0.1$ or less). With the exception of polybutylene succinate, there is a positive correlation of increasing diacid length with melting point and melt enthalpy ($r^2=0.8$ and 0.5 , respectively).

2.1.2.4 Aromatic Polyester Polyols Aromatic polyester polyols are primarily used in the production of polyurethane and polyisocyanurate foams for construction and appliance applications. There are additional applications in slabstock, spray foams, elastomers, and adhesives. Commercially, aromatic polyester polyols are based on diethylene glycol or ethylene glycol and low-molecular-weight PEGs, polymerized with either dimethyl terephthalate, terephthalic acid, phthalic anhydride, or crude recycle scrap of polyester terephthalate (PETr) [54]. In some cases, polyol functionality is increased by addition of trimethylolpropane and pentaerythritol. Of

TABLE 2.4 Properties of selected polyester polyols useful in polyurethane synthesis and comparison to high-density polyethylene

Polyester	Acid	Diol	T_m (°C)	Enthalpy of melting (J/g)
Polycaprolactone	na	na	50	105
Poly-pentadecalactone	na	na	92	182
Polydodecanolactone	na		83	70
Polyundecanolactone	na	na	73	150
Polybutylene adipate	Adipic acid	1,4-Butanediol	55	96
Polyethyldodacanolate	1,12-Dodecandicarboxylic	Ethylene glycol	87	137
Polyhexylnonanoate	Azelaic	1,4-Butanediol	65	141
Polyhexanehexanoic	Sebacic	1,6-Hexanediol	64	123
Polyhexanedodecanoic	1,2-Dodecanoic	1,6-Hexanediol	74	125
Polybutylene succinate	Succinic	1,4-Butanediol	115	96
Polyethylene high density	na	na	133	285

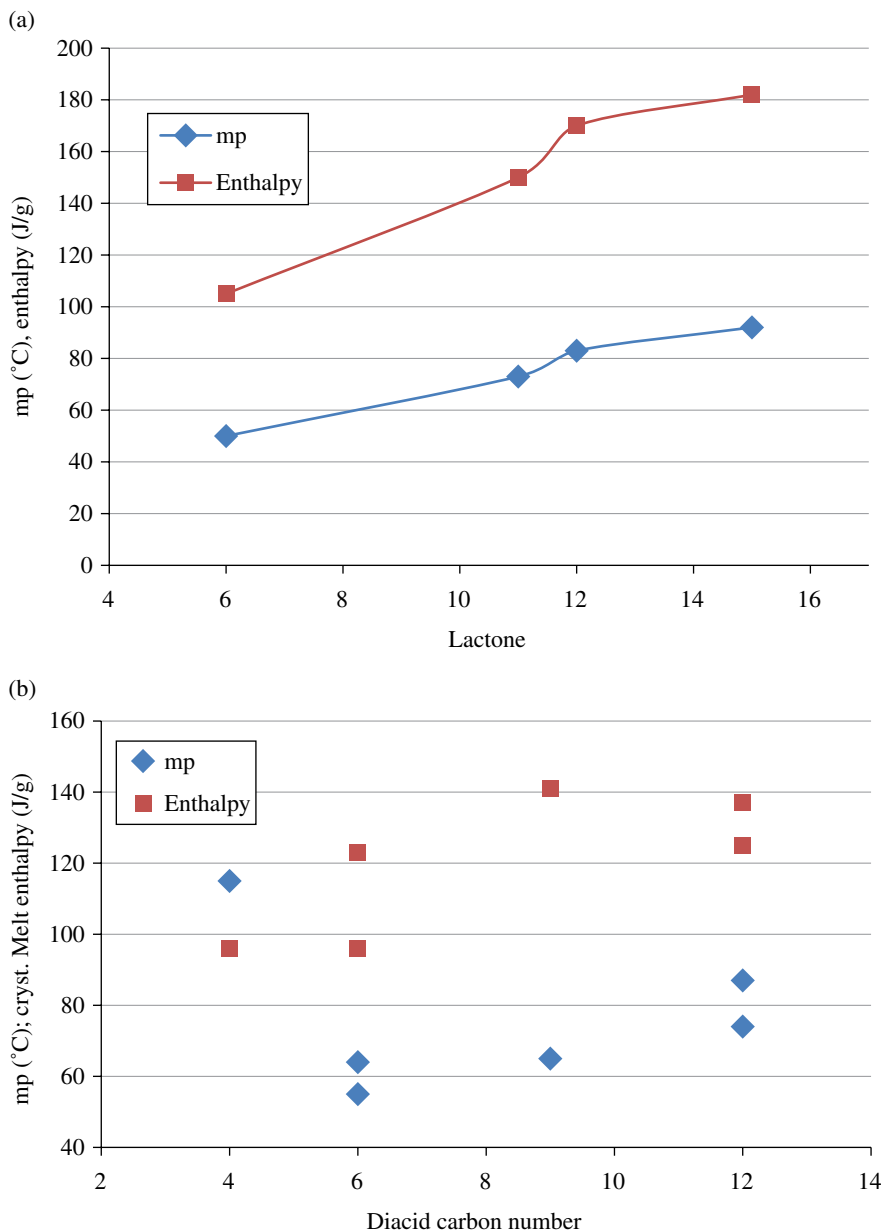


FIGURE 2.24 (a) Melting point and enthalpy of melting of polyester polyols derived from lactone ring opening polymerization as a function of ring size. Properties asymptotically approach those of polyethylene. (b) Melting point and enthalpy of melting for polyester polyols made from condensation polymerization as a function of carbons in the diacid. The trends are somewhat weaker than for the lactone series.

TABLE 2.5 Comparison of polyols used for rigid appliance foam and rigid construction foam

Appliance foams		Construction foams	
Property	Specification	Property	Specification
Functionality	2–2.7	Functionality	2–2.5
Mn (g/mol)	300–600	Mn (g/mol)	300–600
OH# (mgKOH/g)	250–315	OH# (mgKOH/g)	230–350
Viscosity at 25 °C (cP)	2,700–15,000	Viscosity at 25 °C (cP)	2000–5000

Along with differences associated with gel time optimization, construction foams must also meet stringent flammability requirements.

course, any combination of aromatic and aliphatic monomer could be used for making these materials, but price and performance constraints also limit the menu of employable building blocks. The nonnegotiable and established performance and process attributes coupled to high price competition have led to commoditization of this technology [55].

Although the functions of construction and appliance insulation foams overlap, the details differ in some important ways and result in divisions in polyol specifications unique to the two markets. For the appliance market, aromatic polyester polyols are expected to contribute positively to maximizing thermal insulation, minimizing demold postexpansion, and maintaining structural integrity [56]. These attributes are detailed in Table 2.5.

The overlap is significant only in those specific applications where the requirements are the same. In spray foams, it is imperative that the sprayed components foam and build strength very quickly, in a manner similar to that required for appliance foams but for very different reasons. In the appliance sector, there is criticality in being able to process more refrigerators, water heaters, or dishwashers in a shorter time. Also important to appliance manufacturers is that the foam blown into an appliance mold builds strength quickly to prevent deformation from the growing insulation internal gas pressure and not deform from shrinkage upon cooling. For spray foams, designed rapid strength development is a reflection of the desirability that the foam stick to vertical surfaces when necessary.

A critical requirement of construction foams is their flame retardance. It is not expected that the aromatic polyester polyol supply all of this property. The aromatic isocyanate and materials specifically employed to inhibit fire are also employed [57, 58]. However, fire retardance is considered a desirable feature of an aromatic polyester polyol in the construction foam market. The need to spray foam over distances also can limit the foam viscosity of a formulation that a specific application can tolerate. This can in turn dictate the viscosity (and so the structure) of the aromatic polyester polyol used in this application [59]. It also requires in many cases that spray foam applications use significant amounts of low-viscosity polyether polyols in combination with polyester polyols to meet viscosity requirements. Terephthalic acid-based polyester polyols have an increased tendency to crystallize, so using TA-based

TABLE 2.6 Example of an aromatic polyester polyol for construction application

Component/property	Specification
Diacid	Phthalic anhydride
Diol	DEG
Functionality	2
Mn (g/mol)	348
OH # (g KOH/g diol)	330
Viscosity (cP)	2700

TABLE 2.7 Raw materials and unit ratios for two commercial aromatic polyester polyol formulations

Component	Polyol #1	Polyol #2
Phthalic anhydride	0.42	
Terephthalic acid		0.32
DEG	0.58	0.26
PEG 200(Mn = 200 g/mol)		0.42
Free glycol calculated (%)	14.5	24.2
Free glycol measured (%)	15.7	26.2
Viscosity (cP)	2700	630
OH#	330	317

polyesters may be limited by application temperature or may require polyol design considerations that inhibit crystal formation. Table 2.6 is an example of a commercial aromatic polyester polyol available on the market.

Unlike aliphatic polyester polyols, the synthesis of an aromatic polyester polyol may not follow principles for obtaining a defined product of condensation polymerization, but may instead target the properties required for a result. The final product may constitute a designed amount of free DEG, for instance, to obtain the required viscosity or reactivity.

Table 2.7 shows the unit ratios for two commercial aromatic polyester polyols. They are, in principle, the proportions for a diacid reacted with two diols. However, as actually practiced, the desired structure cannot be the calculated structure since polyester product represents an equilibrium, with structures from oligomers to free glycols and acids. The actual distribution of components can be calculated using a Flory–Schulz distribution or measured chromatographically. These methods are usually in good agreement [60]. To meet required properties, it is common to adjust the final polyol with free glycol. In fact, between the two polyols described in Table 2.7, the substantial difference in viscosity is a function of (1) the lower unit ratio of diacid resulting in fewer ester linkages but primarily (2) the higher volume of free glycol in the final product [61, 62].

Since the aromatic polyester polyols are typically lower in molecular weight than aliphatic polyester polyols, there is a higher probability of finding free monomer in

the final product. The free monomers can have a significant effect on the efficacy of the polyol in the final foam product. Product polydispersity in polyester synthesis is an expected phenomenon, but it is wise to measure, or at least calculate, the final product oligomer distribution. This is most easily done using the gamma distribution, or more commonly the Flory–Schulz distribution. The distribution is easily calculated based on knowledge of inputs such as the molecular weight of the repeat unit. The weight average of the Flory–Schulz distribution is calculated from Equation 2.8:

$$W_x = x(1-p)p^{(x-1)} \quad (2.8)$$

where W_x = (weight of all oligomers of weight x /weight of all oligomers) and p is essentially the fraction of converted reactive groups. While the number of monomers present as a fraction of total product weight may be small, their number may be relatively large even at fairly high monomer conversion to product. The number of oligomers as a function of conversion is calculated from Equation 2.9

$$N_x = N_o(1-p)p^{(x-1)} \quad (2.9)$$

The meaning of this distribution is shown in Figure 2.25, where it is seen that except at very high conversion, the mole fraction of monomers in the product polyol can be significant, even when their weight fraction can be quite small. Given the very low equivalent weight, their role in the final polyurethane properties can be important. The figures also illustrate the importance of high conversion percentages in obtaining high-molecular-weight polymers.

The free monomer diol components have a clear and unambiguous role in these polyols. They produce reactive components for the aromatic diacid of the polyol and for the isocyanate component of the subsequent polyurethane foam formulation. Additionally, they provide rheological tuning to the polyols. Beyond that, they also provide a means of improving compatibility of the components of the formulation. Lastly, as the cost of the diols is usually lower than that of the diacid, the diols can provide a means of managing overall product cost. Artful combinations of diols can, in principle, provide a means of performance innovation by improving properties at reduced cost.

The diacid components, terephthalic acid (or dimethyl terephthalate), and phthalic anhydride have significant effects on cost as well (isophthalic acid is rarely used due to cost considerations). In turn, they also exert a subtle effect on properties due to their different structures. Cost is affected by the so-called unit ratio of the building block—essentially a determination of mass equivalence for the different molecules within an equivalent final product. Although all final products are either identical (using terephthalic acid or dimethyl terephthalate) or isomeric (using phthalic anhydride), the differences relate to the molecular weight of the building block diacid and the mass of condensation product produced (Fig. 2.26). By this measure, phthalic anhydride is the most cost-effective aromatic unit; however, it is usually almost 20% more expensive than terephthalic acid resulting in supply issues usually being the deciding factor for which is used.

In addition, there are differences between the terephthalate residues and orthophthalic residues from phthalic anhydride (Fig. 2.27). The substitution pattern has a

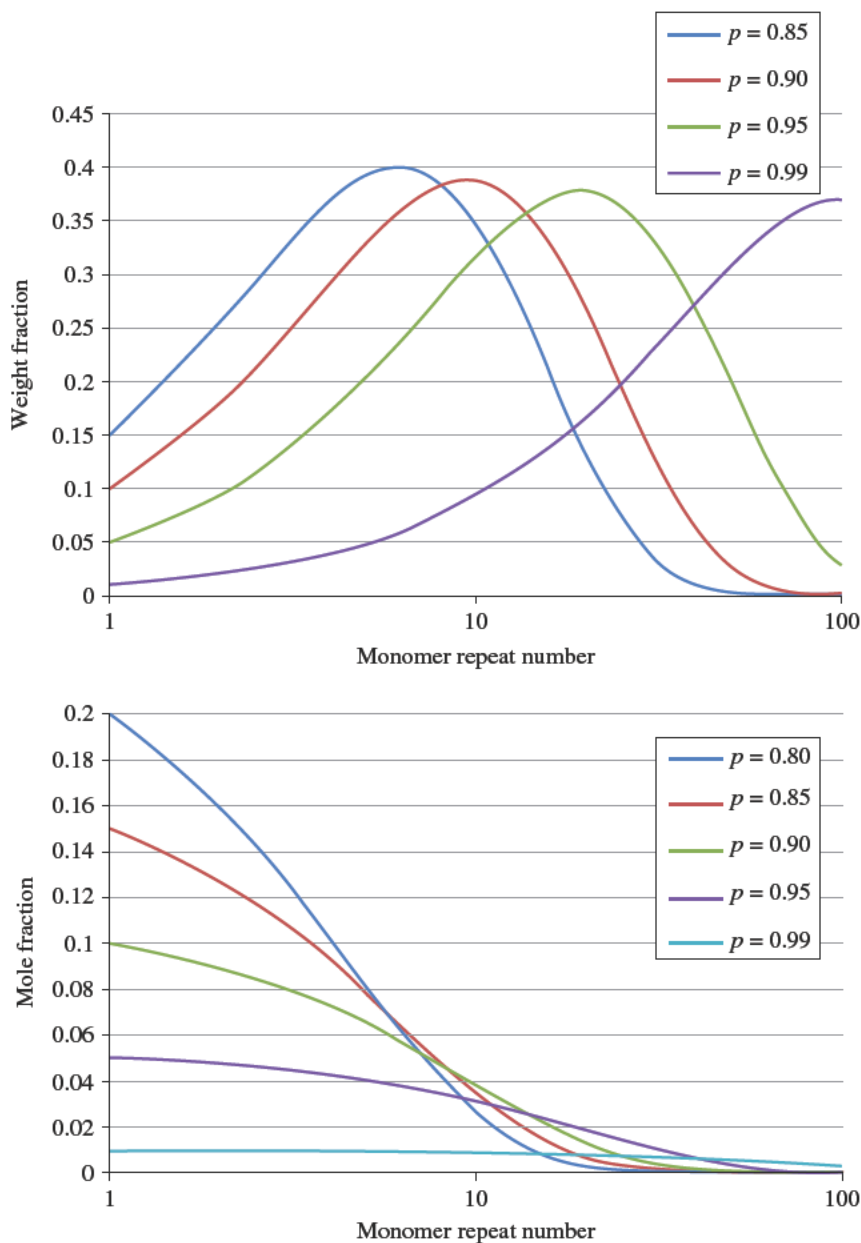


FIGURE 2.25 Weight and number average distributions of oligomer sizes present in a polyester synthesis based on the Flory-Schultz distribution. (See insert for color representation of the figure.)

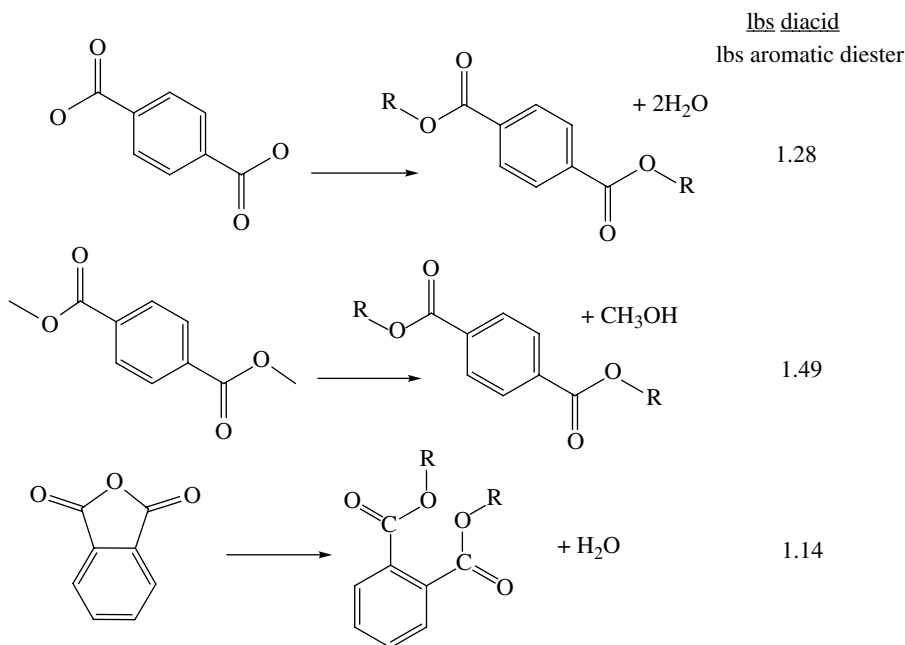


FIGURE 2.26 Unit ratios for diacids or diesters used in preparation of aromatic polyester polyol synthesis.

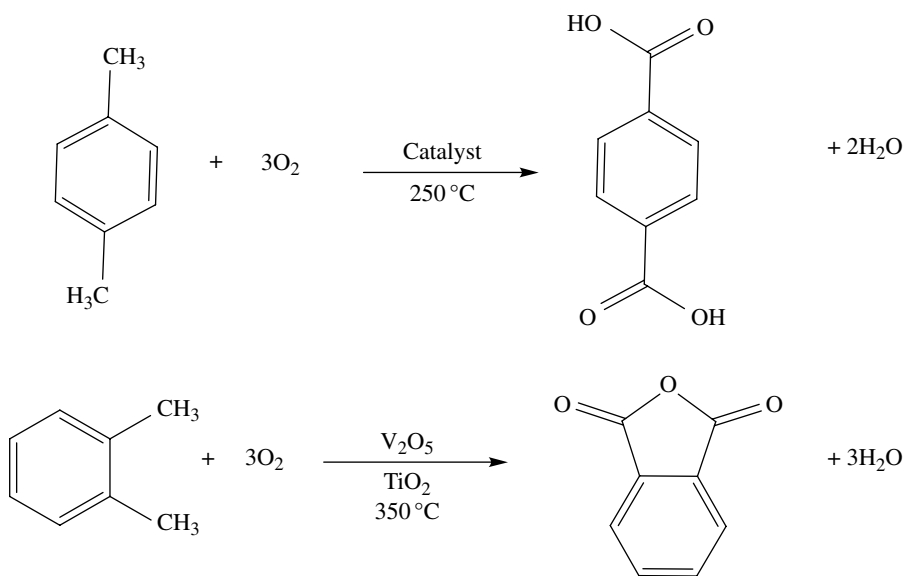


FIGURE 2.27 Production of terephthalic acid and phthalic anhydride.

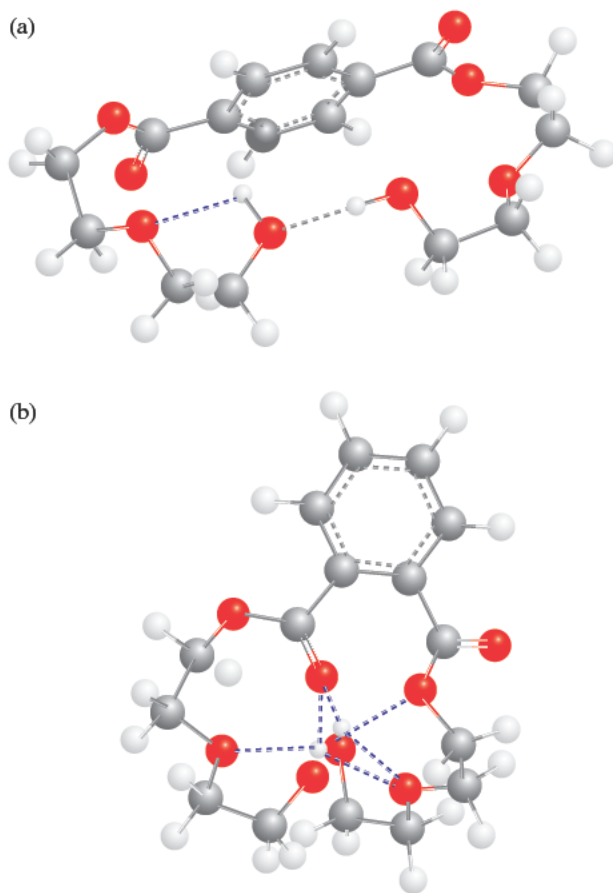


FIGURE 2.28 Comparison of lowest energy conformations of aromatic polyester polyol from (a) terephthalic acid and (b) orthophthalic acid (or phthalic anhydride) and DEG. The free volume requirement of the ortho positional substitution is much higher which may account for much of the viscosity difference between polyols made with the different co-monomers. (See insert for color representation of the figure.)

substantial effect on free volume requirements of the polyol component, which in turn has an effect on subsequent rheological properties. Figure 2.28 shows energy minimized structures for the aromatic polyester polyol of DEG with terephthalic (a) and (b) orthophthalic acid with approximately equal energies accounted for by hydrogen-bonding interactions and overall conformational energies. It is clear that the aromatic polyester polyol from orthophthalic acid requires additional free volume due to the pendant benzylic residue but in turn allows more intramolecular van der Waals interaction between ether moieties. While the aromatic positional isomer is known to affect foam properties, it has not previously been associated with fundamental chain physics, and the causal relationship has been lacking [63].

TABLE 2.8 Properties of rigid polyurethane foams with aromatic polyester polyols having either terephthalic acid or phthalic diacid comonomers reacted with DEG

Diacid	Terephthalic acid	Phthalic anhydride
Viscosity (cP)	4000	2700
λ mW/mK at 10 °C	19.6	19.85
Compressive strength kPa	99	96
Weight loss upon burning (%)	27	32

Viscosity data refers to the viscosity of the polyols used in the formulations. Other foam formulation factors were held constant.

Lastly, aromatic positional isomers are also associated with small but real differences in performance (Table 2.8). While the origins of these differences are not established, it emphasizes the role of positional isomers in establishing structure/property relationships [64].

2.1.3 Other Polyols

2.1.3.1 Polycarbonate Polyols In application to polyurethanes, polycarbonate polyols are among the highest performance polyol backbones available in the marketplace [65, 66]. They are also among the most expensive and produced at relatively small volumes. The world capacity for polycarbonate production is approximately 60 million pounds and consumption in 2010 was approximately 50 MM lbs [45]. Relative to other polyols, the properties most attractive about polycarbonate polyols are thermal, UV, and hydrolytic stability. This suite of attributes has resulted in polycarbonate polyols finding their widest application in very-high-performance applications of coatings, elastomers, and adhesives.

Preparation of Polycarbonate Polyols The preparation of polycarbonate polyols is straightforward in its simplest form. It is the reaction of phosgene or a carbonate monomer, usually dimethyl carbonate (DMC) with a diol monomer or a mixture of diol monomers (Fig. 2.29). In the case of the phosgene route, the liberated hydrochloric acid (HCl) is usually quenched with NaOH to form the filterable salt. This route is generally discouraged due to the significant environmental health and safety drawbacks associated with large-scale handling of phosgene.

DMC is a relatively more attractive reagent for polycarbonate synthesis because of its low molecular weight, its relatively high unit ratio in the polymerization, and its relatively low cost and ready commercial availability. One disadvantage of using DMC is the evolution of toxic methanol requiring safety protocols in production. A more significant issue is the 30/70 DMC/methanol azeotrope that forms resulting in lost DMC in the condensation product [67, 68]. The practical effect is to make usage of DMC quite inefficient since the methanol/DMC azeotrope is difficult to separate by normal methods [69]. One approach is to determine the minimum in the

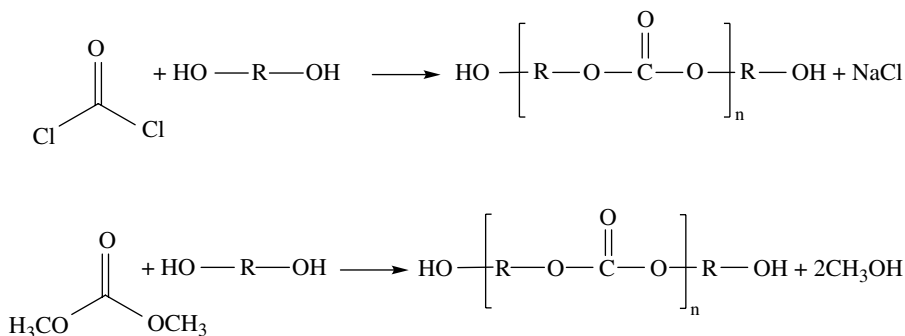


FIGURE 2.29 Preparation of polycarbonate polyols from phosgene (not recommended) or dimethyl carbonate.

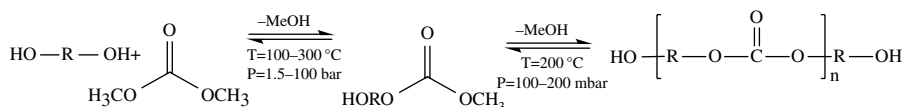


FIGURE 2.30 Preparation of polycarbonate polyols using an elevated pressure procedure.

DMC/MeOH concentration in the azeotrope as a function of temperature. The reaction is then run controlling the reaction vessel to the temperature, producing overhead products at the minimum of DMC in the azeotrope. However, this approach can be unworkable from a practical standpoint since the boiling point of DMC is about 90°C , a temperature at which the reaction rate between the diol and the carbonate is very low. Thus, one efficient procedure for preparation of polycarbonate polyols using DMC is to run the reaction vessel at the optimum temperature for reaction, which at the same time optimizes the use of DMC by minimizing its content in the azeotrope-collected overhead. This can be accomplished by slow feeding (“starve feeding”) the DMC to the molten rapidly mixing diol. The optimum overheads temperature is about 58°C . The exact conditions for this will depend on the geometry of the reaction vessel, the control of reaction vessel heaters, and the mixing of the reaction vessel.

An alternative efficient method for producing polycarbonate polyols is to perform the reaction at elevated pressure. The reaction is performed in an autoclave with all components of reaction present (Fig. 2.30). The temperature and pressure are elevated with the purpose of driving the reaction to a stage at which a large amount of DMC has been converted to carbonate diol adduct. Subsequently, the pressure and temperature are reduced to drive the reaction to completion by removal of methanol. While still inefficient in DMC, this method provides improved time to a final product and does so in a smaller production footprint [70].

An alternative polycarbonate polyol is the polyalkylene carbonate formed from the reaction of oxiranes and CO_2 . A common problem associated with this synthesis has been the formation of five member cyclic carbonates. There has been recent

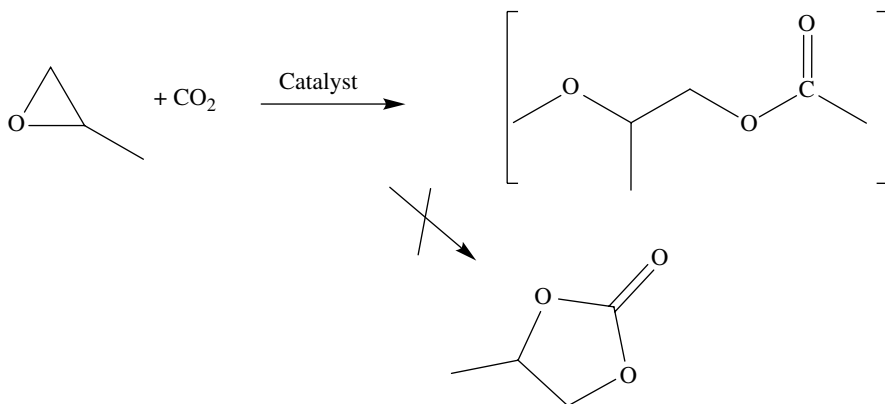


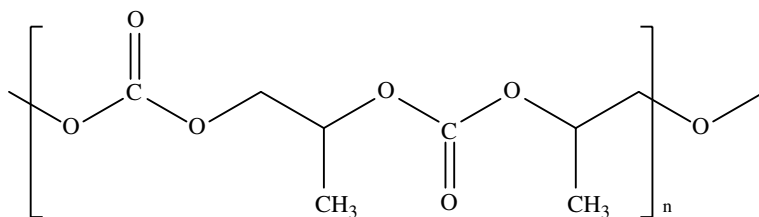
FIGURE 2.31 Preparation of polycarbonate polyol using an alkoxyolate.

activity with new catalysts that have proven themselves able to result in high-molecular-weight polycarbonate polyols (185–250 kDa) and low-molecular-weight polyols useful in PU synthesis (Fig. 2.31) [71, 72]. Despite the low cost of the building blocks, pricing of these materials is approximately the same as those achieved via condensation techniques described earlier.

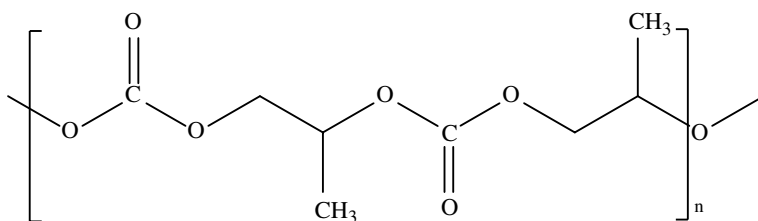
There are numerous catalysts for this polymerization, heterogeneous and homogeneous, varying by efficiency, tendency to form the undesired cyclic carbonate, and resulting tacticity of the final polyol product. The tacticity is one of several controls of polyol structure that can be used to design final properties of polypropylene carbonate polyols (Fig. 2.32).

Design of polycarbonate polyol structure is primarily a matter of choice of which diol or mixture of polyols to react with the carbonate linkage. Designed artfully, the properties of the resulting polycarbonate polyol can be varied widely and have considerable effect on a derived polyurethane property. Table 2.9 is a list of diol monomers polymerized with DMC to make polycarbonate polyols, typical applications, and the physical state of the polyol produced. Hexanediol is a preferred monomer due to its reduced tendency to volatilize during polymerization (compared to 1,4-butanediol). It is also apparent that diol additives that randomize or disrupt regular chain structure help make the polyol liquid.

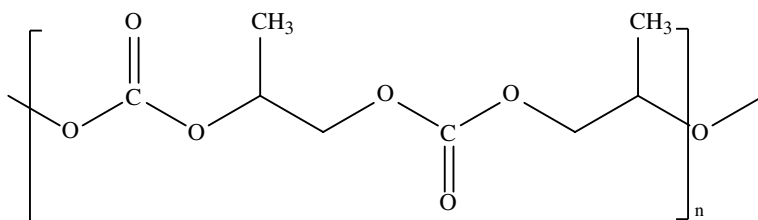
2.1.3.2 Polyacrylate Polyols Acrylic polyols differ in numerous ways from the polyols described in the previous text, but they are an important and common occurrence in our day-to-day experience. Unlike the previously described polyols, which we may find ourselves sitting upon, walking upon, wearing, and depending upon in numerous but silent functions, acrylic polyols in isocyanate formulations are generally limited to coatings and particularly, but not exclusively, to automotive surface finishes [73–75]. In addition, acrylic polyols find application in wood coatings and anticorrosion finishes. Acrylic polyols are preferred for achieving higher hardness, UV stability, and water and acid stability. In contrast, polyester



Head-head



Head-tail



Tail-tail

FIGURE 2.32 Polycarbonatepolyols from alkoxyates and the structural variation that can manifest due to addition mechanism.

polyols are preferred in the same applications where solvent resistance, toughness, and flexibility are critical. Polyesters may find application for the same applications where hydrolytic stability is less important and cost is paramount. As commonly used, almost 200 thousand metric tons (440 million pounds) of acrylic polyols were used worldwide in 2012, with an average annual growth rate of over 4%, tracking the overall use of urethane surface coatings [76, 77]. As in all of these numbers, the use and growth rates are not globally homogeneous.

Preparation of Acrylic Polyols Acrylic polyols are prepared like many acrylics, via radical initiation. Any acrylic monomer may be used as long as hydroxyl functionalized monomers such hydroxyethyl methacrylate, hydroxy butylacrylate, hydroxyethyl acrylate, etc. are present in the backbone [78]. The role of any particular

TABLE 2.9 Select polycarbonate polyols (based on diol variation) and the difference in properties

Diol	Characteristics	Applications
1,6-Hexanediol	750 Da, solid	Coatings, lenses
1,6-Hexanediol	1000 Da, waxy solid	Coatings
1,6-Hexanediol	2000 Da, waxy solid	Adhesives, artificial leather
1,6-Hexanediol	3000 Da, solid	Artificial leather
50/50 1,6-hexanediol/ 1,5-pentanediol	2000 Da, liquid	Adhesives, artificial leather
1,6-Hexanediol/ polycaprolactone	2000 Da, liquid	Adhesives
1,6-Hexanediol/ 1,4-cyclohexane dimethanol	1000 Da, solid	Adhesives
2,2-Butyl, ethyl 1,3-propanediol	1000 Da, liquid	Elastomers, flexible coatings
2,2-Butyl, ethyl 1,3-propanediol	2000 Da, liquid	Elastomers, flexible coatings
1,3-Propanediol	2000 Da, solid	
Adipate polyester cohexanediol polycarbonate	2000 Da, liquid	Elastomers, adhesives

acrylic monomer in the preparation of an acrylic polyol would be the same as in any acrylic resin: to adjust glass transition temperature, hardness, flexibility, or barrier properties. Styrene is also commonly used in acyclic polyol synthesis to increase hardness. Polar nonhydroxy components such as acrylic acid and acrylonitrile can be used to increase interchain polar interactions and so increase the tensile strength and ultimate elongation of a resin at the potential cost of decreasing low temperature flexibility [79]. Allyl alcohol has been employed as a monomer for modification of molecular weight. Depending on the application, the molecular weight of acrylic polyols can vary from under a thousand to several thousand with hydroxyl equivalent weight from several hundred to several thousand. To maintain control of the polymerization process and maximize conversion of monomer to polymer, the polymerization is usually performed in a solvent such as ethyl acetate or an aromatic such as xylenes. The solvent can then be removed, or be used as a solvent for subsequent application of the coating. The carrier solvent aspect of acrylic polyols has become an area for technological innovation as producers try to limit solvent content and reduce regulated volatile organic carbon (VOC) emissions. Common initiators for acrylic polymerization such as peroxides are also commonly used in this process. An illustrative formulation and polymerization product is shown in Figure 2.33. In an actual formulation, the butyl acrylate and styrene could be balanced to provide the desired level of flexibility and hardness for the given application. The amount of hydroxyl functionalized acrylate would be balanced to provide the desired cross-link density for the coating.

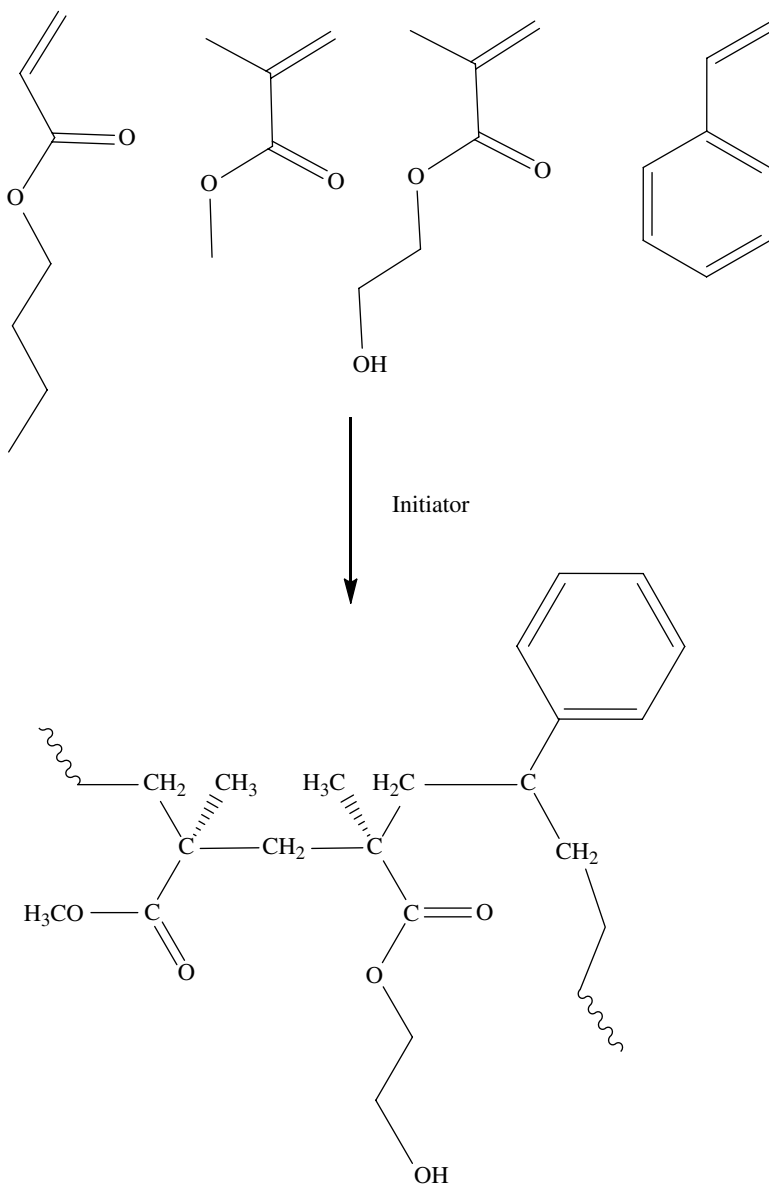


FIGURE 2.33 Example preparation of an acrylic polyols.

Acrylic polyols have also been designed to optimize compatibility with aqueous systems. This is normally done by including acrylic acid among the monomers [80]. The acid is subsequently neutralized with an amine such as dimethyl ethanolamine and water. The ratio of monomers will control the final properties of the film as well as the differential solubility.

2.1.4 Filled Polyols

The low cost and ubiquity of polyols has generated innovation in features and additives to add value to downstream polyurethane processing. One innovation has involved using the polyol as a polymerization medium and then using those polyol–copolymer mixtures to provide a downstream value. Three so-called copolymer polyols have been developed and found significant commercial value. These are (i) styrene–acrylonitrile (SAN)-filled polyols [81], referred generically as copolymer polyols, prepared via radical polymerization of vinyl monomers; (ii) step growth copolymer polymerizations of isocyanates and amines like hydrazine called *polyharnstoff dispersion* (PHD) polyols [82]; and (iii) *polyisocyanate polyaddition* (PIPA) polyols made by reaction of an isocyanate and an alkanolamine like triethanolamine (TEA) [83]. PHD polyols result in a polyurea filler phase, and the PIPA process results in a urethane-dispersed phase. Copolymer polyols are commonly used in comfort applications such as seating where it is used to provide increased load bearing without having to increase overall foam density. As a result of the improved load bearing, the foam will also exhibit less shrinkage upon cooling due to its inherent ability to resist shrinkage stresses. In these roles, the combined copolymer polyol market was approximately 650,000 metric tons in 2010, growing at about the rate of the automotive industry. In use, the critical characteristics sought by customers is the percent polymer in the polyol (the solid level), viscosity of the filled polyol, filterability or polymer-phase uniformity, and final product characteristics such as color, VOC, and odor minimization. Virtually all producers of polyether polyols sold into comfort seating applications also offer filled polyol options to their customers.

2.1.4.1 Copolymer Polyols The polymerization of styrene and acrylonitrile to form SAN in polyol was first documented by Stamberger in the 1960s [84]. The polymerization is easily accomplished using AMBN 2,2'-azodi(2-methylbutyronitrile) or AIBN as an initiator for the radical polymerization (Fig. 2.34).

The limited solubility of SAN in polyol causes it to phase separate into domains capable of scattering light. This results in filled polyol being milky white. The phase-separated polyol phase is referred to as the serum since it still contains SAN polymer and oligomers up to the solubility limit. During the polymerization, the radical initiators may abstract hydrogen from the polyol, particularly the hydrogen on the tertiary carbon of polypropylene oxide, and provide a radical site on the polyol chain (Fig. 2.35). These carbon-centered radicals provide new initiation sites

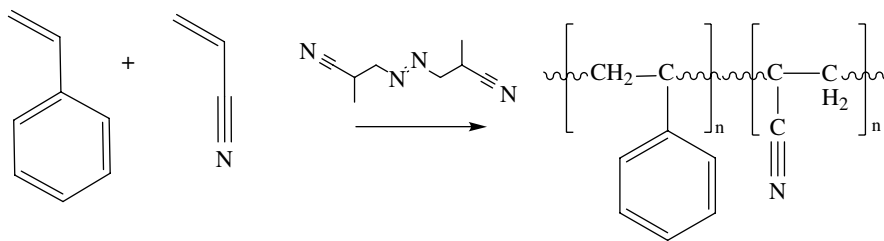


FIGURE 2.34 Polymerization of SAN using azobisisobutyronitrile (AIBN) as an initiator.

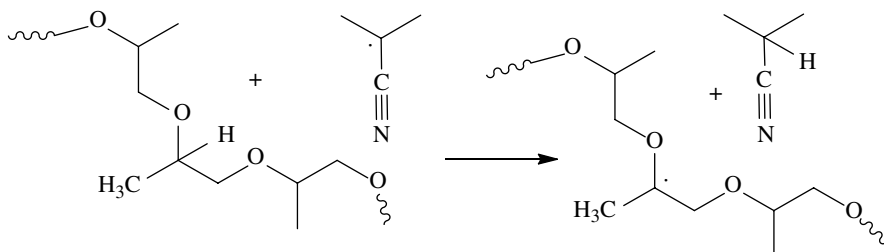


FIGURE 2.35 Generation of a carbon centered radical on a propylene oxide polyol. The radical center can serve as a polymerization initiator or chain terminator.

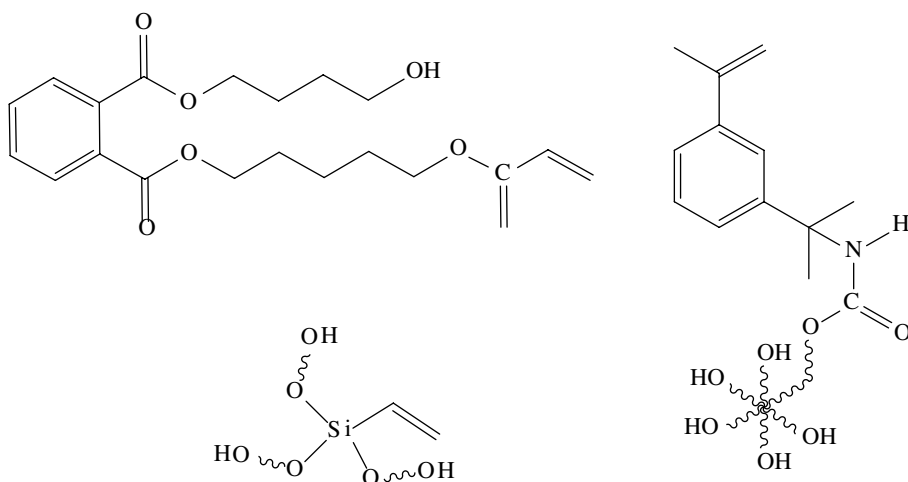


FIGURE 2.36 Examples of macromer structures.

for radical polymerization of SAN polymer and create a graft stabilization mechanism keeping the SAN dispersed in the polyol [85]. The polymer in the serum causes the viscosity of the filled polyol to increase such that it has a useable limit of 20–25% solids before it becomes unusable to foam manufacturers due to poor flow and mixing with other foam components having significantly lower viscosity.

Continuing innovation has focused on achieving ever smaller particles, low color formation, higher solids at lower viscosity, and improved VOC profile. Polyol viscosity, directly related to solid content, has been an area of particular innovation and patent activity. Breakthrough performance has been established by the development of stabilizers or “macromers” (macromolecular monomers) [86]. These molecules typically are A–B functional monomers with vinyl and hydroxyl functionality. While reacting readily into the SAN polymer structure, they can provide a new stabilization mechanism, preventing agglomeration or settling, without requiring the formation of radical sites on the polyol chain. Typical macromer structures are presented in Figure 2.36. The hydroxyl functionalization is related structurally to the host polyol, while the vinyl component is polymerized with a short SAN chain. Artful design of

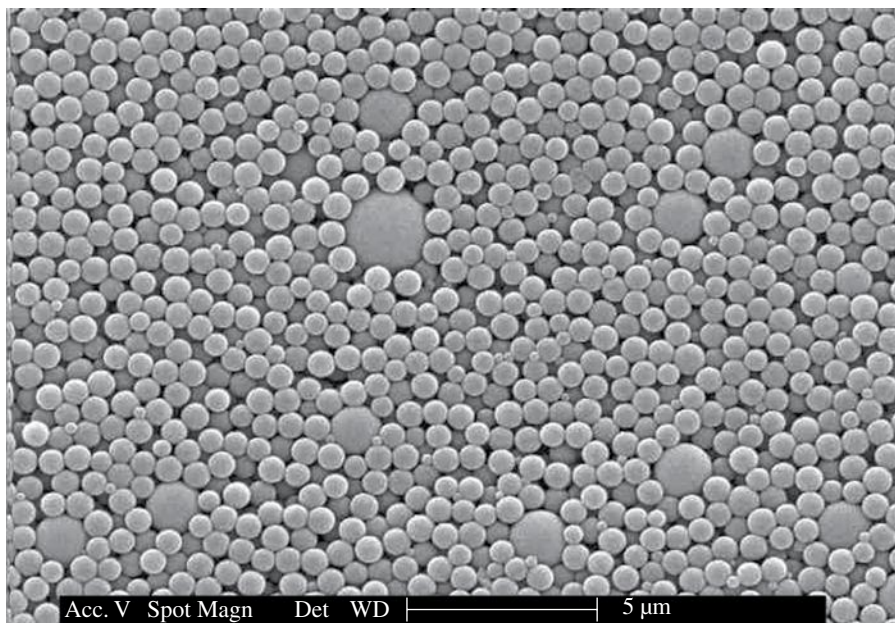


FIGURE 2.37 Scanning electron microscope image of particles formed in co-polymer polyol synthesis. The particle size uniformity points to the exquisite control and optimization of the process. Image by Robert Vastenhout; The Dow Chemical Co.

macromer structures, polyol design, and processing have allowed solid contents greater than 50% solids, with viscosities of ca. 5000 mPas, and weight average particle sizes under 1 μm (Fig. 2.37). The copolymer polyols have adjusted hydroxyl equivalent weight of between 2500 and 3000 g/OH eq. The polyols usually used for dilution in foam formulation are high-functionality polyols with equivalent weight between 1500 and 2000 g/eq. The polyols are usually EO-capped PO polyols with 15–20% EO content to assure rapid polyurethane formation in molded foam operations.

2.1.4.2 PHD Polyols PHD polyols are prepared for the same reason that copolymer polyols are: to provide a stable filler phase for flexible foams with greater load bearing at low density [87]. PHD polyols are created by rapid reaction of polyisocyanates, usually toluene diisocyanate (TDI), with low-molecular-weight polyamines or hydrazine in a polyol phase. While reaction of isocyanates with amines is much faster than that of isocyanates with polyol hydroxyls (see Chapter 3), there is sufficient urethane formation with the polyol to create a stabilization mechanism for the formed particles.

A continuous process for making PHD polyols generally involves impingement mixing of the components. Batch descriptions have been described and economic analyses presented [88]. The process involves rapid addition of TDI to hot (80 °C) aqueous hydrazine dispersed in a polyol used for molded foam applications under vigorous mixing conditions. The stoichiometry is such that isocyanate functionality

exceeds amine functionality to insure reaction with the polyol phase and militate against the need for system neutralization. The heat of reaction is a major source of control and manufacturing attention. Subsequently, the system is dehydrated under heat and vacuum.

The reaction of isocyanates with amines is 1000 times faster than their reaction with primary hydroxyls (see Chapter 3). Thus, the PHD polyol reaction does not promote the level of compatibilization and size limitation available with the copolymer polyol process that employs macromer stabilizer technology. Additionally, the rapid amine–isocyanate reaction results in poor control of particle nucleation and formation. The high concentration of reactants in the initial stages results in many initial nuclei but also diffusion-controlled reaction and growth. The result is a relatively broad distribution of particle sizes. The low concentration toward the end of the reaction results in the formation of fewer and smaller particles with an increased incidence of polyol reaction (abetted by the high temperatures of the reaction at the end). This usually results in PHD polyols exhibiting bimodal distribution or a broad monomodal distribution of particle sizes from hundreds of nanometers to several micrometers. Additionally, viscosities of PHD polyols tend to be somewhat higher than the SAN copolymer polyol. The causes of this effect are not completely understood but probably result from a significant amount of particle–polyol colloidal interaction resulting in less free polyol in the system and very small particles acting as chain extenders increasing the effective molecular weight of the fluid phase. The effect is not huge, and process improvements have been able to produce 30% solid PHD polyols in the same viscosity realm (~3000–4000 cP) as those from 40% solid SAN copolymers [89].

Like SAN copolymers, most PHD products are spherical morphology. A less desirable, though still interesting, result can occur to form rods of polyurea-phase dispersion. The less desirable aspect is that the high aspect ratio dispersion particles can significantly increase the viscosity of the solution due to increased opportunity for particle–particle interactions. On the other hand, higher aspect ratio particles can significantly increase the load-bearing efficiency of PHD polyols that would then be incorporated into the subsequent foam. The different morphology can result by controlling the disposition of isocyanate and amine phases within the polyol-reacting medium. In the case that the solid phase forms either interfacially or due to two-phase (amine–isocyanate) interdiffusion, the typical and desired (from a low-viscosity standpoint) spherical particle is obtained. In the case that the solvent polyol acts as an intermediating and diffusion rate controlling medium, it becomes possible to obtain rodlike structures.

2.1.4.3 PIPA Polyols PIPA polyols are related to PHD polyols except that polyurethane rather than polyurea filler phase is produced in a polyol. The process is relatively simple, and several foam producers are known to produce it for captive use rather than purchase alternative-filled polyols. The chemistry is relatively straightforward, though optimization requires significant control. The particle is produced through the reaction of a polyisocyanate such as TDI with a short-chain polyol such as TEA as illustrated in Fig. 2.38. The polyol, the TEA, and the catalyst are premixed,

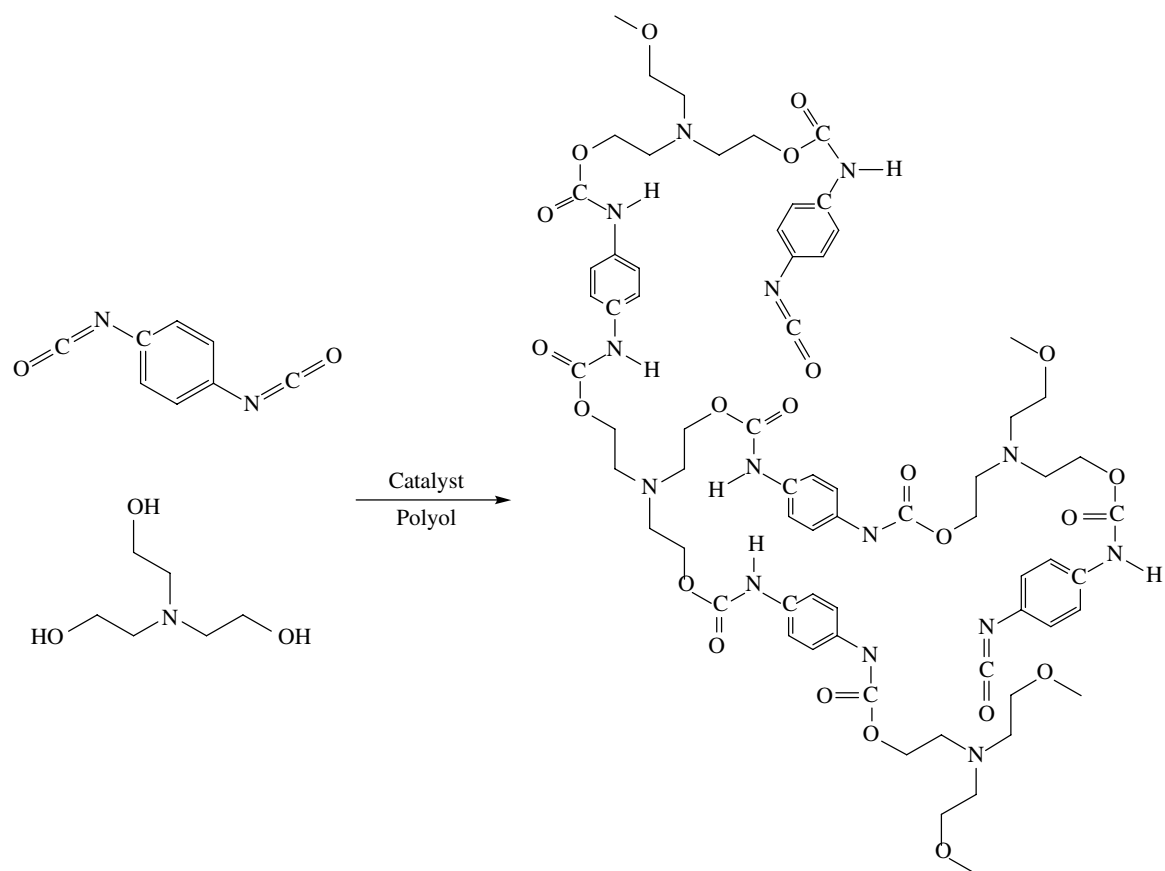


FIGURE 2.38 Preparation of a PIPA polyol.

and the TDI is added rapidly with vigorous mixing [90]. As the particle forms in the polyol medium, it can exceed its solubility limit and precipitate. Surface isocyanate groups allow for continued growth of the particle from reaction with TDI and TEA though this occurs at a slower rate. In addition, at all times, free isocyanate groups can react with hydroxyl functionality from the polyol. In fact, if the isocyanate reaction with the polyol is not closely controlled, undesirable properties are obtained. For instance, if the polyol reaction is encumbered by the presence of too many polyol secondary hydroxyl end groups, the particles will not stabilize in the polyol medium and will develop a size distribution with large average size. If there is too much reaction with the polyol, the size distribution will be small, but the filled polyol will have a very high viscosity.

In practice, this problem is controlled via a technique commonly employed in latex emulsion polymerization, which is to seed the medium prior to isocyanate addition. Thus, to the base polyol–TEA–catalyst, an addition is made of small seed particles in the base polyol. When the TDI is added, particle formation begins preferentially on the suspended seeds, resulting in a high density of preformed uniform nucleation sites from which the PIPA particles can grow. The result is a significantly more uniform particle distribution centered at smaller sizes. The reaction of base polyol on the seed isocyanate surface also serves to limit the further growth of the particles. Controlling the concentration of seed particles and the size and distribution of seed sizes in the initial state helps obtain an optimum final result.

2.1.5 Seed Oil-Derived Polyols

The convergence of advanced industrial biotechnology and advanced chemical manufacturing techniques has opened up an opportunity to develop agricultural-based polyol feedstocks. Whereas most polyols are originally derived from C_2 and C_3 components of natural gas, the use of seed oils provides an additional source of hydrocarbon with either intrinsic hydroxyl functionality or with an olefin reactive handle to create isocyanate reactive groups. Modern agrosience has at the same time been developing genetic variants that more ideally suit chemical industry requirements for cost-competitive feedstocks. Table 2.10 provides a list of seed oils and their fatty acid composition [91]. The fatty acid compositions can vary around these average values depending on the soil and growing conditions. There are many other seed oils that have been the subject of their potential for use in making polyols based on availability or uniqueness of fatty acid composition. Figure 2.39 shows the structure of the fatty acid components. The seed oil contains the fatty acid components in the form of a triglyceride (Fig. 2.40). The triglyceride can be modified for use from its native form by transforming the olefin groups to hydroxyl groups, for instance. Alternatively, the fatty acids can be freed of the glycerine via alcoholysis or hydrolysis to form the ester or acid, respectively [92]. If the native triglyceride is used, the hydroxyl equivalent weight of the polyol will be the molecular weight divided by the average hydroxyl functionality on the triglyceride. The molecular weight between cross-links in the final

TABLE 2.10 Fatty acid composition of common seed oils used for polyester polyol synthesis

Fatty acid composition (%)	Soy	Sunflower	High oleic sunflower	Canola	Modified canola	Castor
Palmitic	11	6	3	4	4	1
Stearic	5	5	1	2	2	1
Oleic	22	18	93	61	78	5
Linoleic	54	69	1	21	13	2
Linolenic	8	2	0	11	2	1
Ricinoleic						90

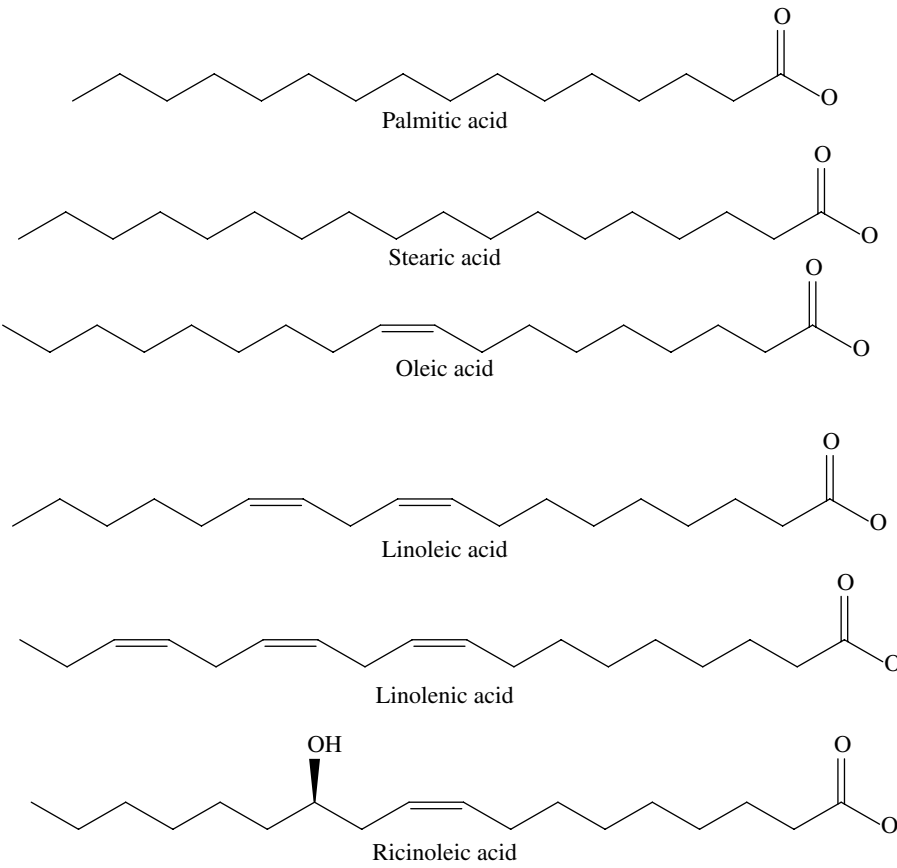


FIGURE 2.39 Structure of fatty acid components of seed oils.

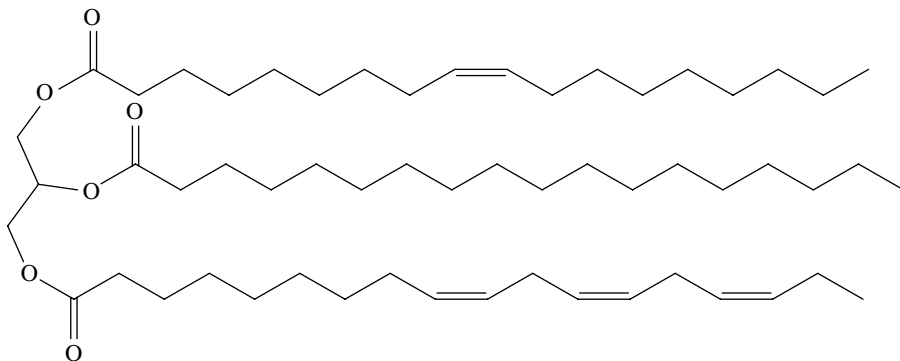


FIGURE 2.40 Illustrative triglyceride structure showing oleic, stearic and linolenic esters.

polyurethane will be very inhomogeneous as some arms of the triglyceride will be stearate or palmitate and have no hydroxyl functionality, and some may have as many as three hydroxyls with only a few carbon atoms between them.

Castor oil from the castor bean is a unique substrate since it is the triglyceride of ricinoleic acid, which, as can be seen in Figure 2.39, is already hydroxyl functionalized. This allows the unmodified castor oil to be used in some applications with no thermochemical transformation required [93].

2.1.5.1 Preparation of Seed Oil-Derived Polyols Epoxidation and Ring Opening There are numerous ways to create functionality on the seed oil internal olefin bonds for use in polyurethane chemistry. One of the simplest methods is to ring open epoxidized seed oil with ring-opening reagents such as methanol and HCl to produce hydroxy functional esters. Epoxidized soybean oil and linseed oil have been converted this way and tested in rigid foam applications, but performance issues have generally limited their application [94]. A related but more complicated method involves alkoxylation of ring-opened epoxidized seed oil. The epoxides are ring opened with a diol such as ethylene glycol and subsequently alkoxyated to the desired structure (Fig. 2.41). These structures have found use by virtue of the reactivity provided by the primary hydroxyl product [95].

Ozonolysis Ozonolysis is a seed oil modification technique that opens avenues to numerous polymerization building blocks. Ozonolysis of the fatty acid double bonds creates ozonide functionalities that can be subsequently reacted to diacids, acid aldehydes, terminal acids, and terminal aldehydes [96]. The difunctional materials can then be modified for convenient polymerization for polyurethanes. While attractive for its versatility and seeming simplicity, the number of steps necessary to get to useable polymerization feedstocks can be a roadblock to economic feasibility. Figure 2.42 shows the pathways available to polymerization building blocks from ozonolysis of oleic acid [97].

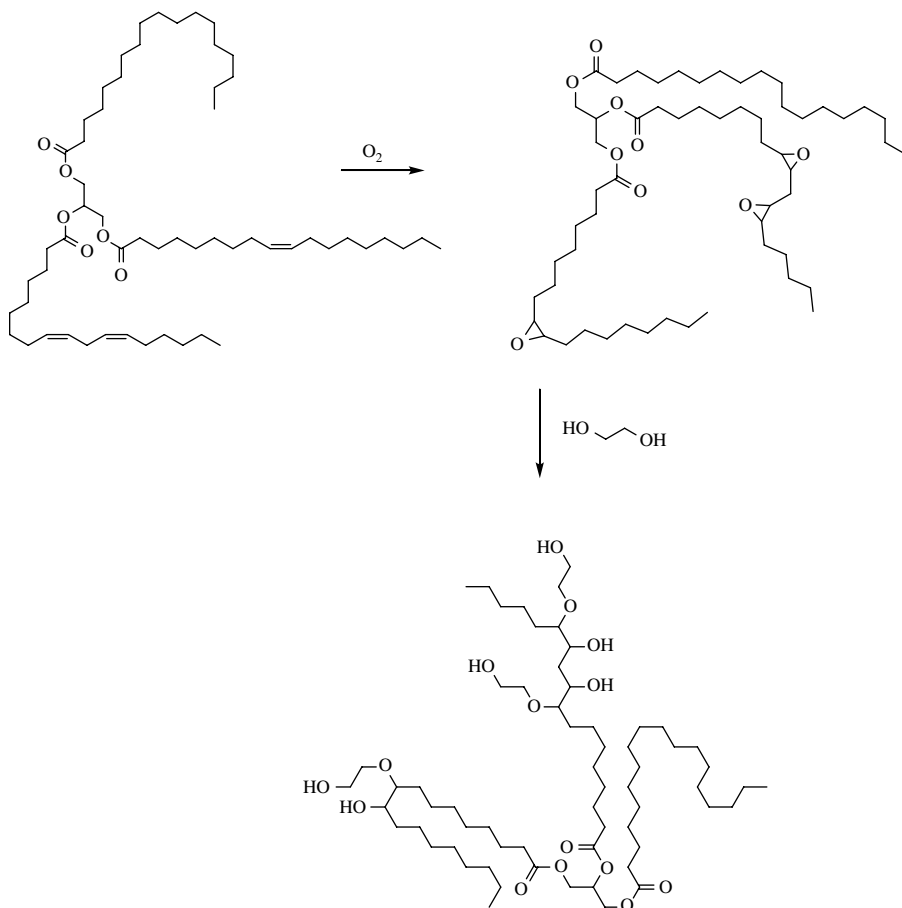


FIGURE 2.41 Oxidation of a triglyceride to the epoxidized form followed by alcoholysis to the ester alcohol of the triglyceride. The alcohols can react subsequently with isocyanates to form urethanes.

Hydroformylation and Reduction Hydroformylation of seed oil unsaturation forms an aldehyde at each olefin group, which can then be reduced to form a primary hydroxy methyl group in place of each aldehyde. This technology has the benefits of quantitatively producing a single primary hydroxyl group for every olefin resulting in polyester polyol building blocks with uniform reactivity [98]. The hydroformylation of the olefin to the aldehyde is accomplished with very expensive homogeneous rhodium catalysts that must be recovered by quantitative extraction, or the product can quickly become very expensive to produce. Reduction of the aldehyde can be accomplished by any number of well-known industrial reduction procedures. When this procedure is applied to the triglyceride, the equivalent weight of the polyol is on the order of 300 g/OH group. This equivalent weight is useable in rigid foam formulations but might require formulation with

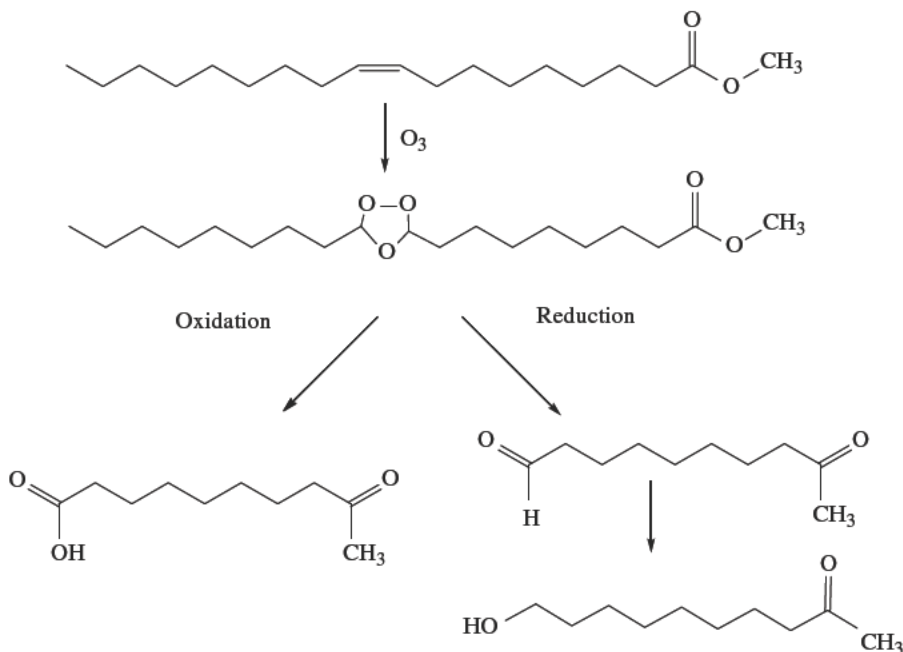


FIGURE 2.42 Simplified ozonolysis of oleic acid. Other products are also possible [97].

even lower equivalent weight polyols to provide the necessary cross-link density to result in rapid gelation, high tensile strength, and low gas transmission necessary for most rigid foam applications.

It is also possible to separate the fatty acids from the triglyceride to produce the fatty acid or the methyl ester. Hydroformylation and reduction then result in an A-B monomer having ester and hydroxyl functionality on a single monomer (Fig. 2.43) [99].

Using a low-molecular-weight polyol as a polymerization starter or "initiator," it is thus possible to obtain a polyester polyol of nearly any molecular weight or functionality typical for flexible applications. Separation of the different hydroformylation and reduction products resulting in diol and triol esters, for instance, can allow for each product to find its highest value application.

Along with the process requirements associated with catalyst recovery, several issues can pose as obstacles to this elegant procedure. One problem is that, even with substantial optimization, the overall cost can be prohibitive due to the number of steps necessary to get from seed oil to final building blocks including separations and recycle. Another potential problem is related to the saturates content found in most seed oils, the presence of which reduces overall asset utilization by occupying volume in the chemical process but on which no modification occurs [101]. The stearate and palmitate saturates furthermore serve no useful role in polyurethane chemistry and therefore will either degrade performance or require finding an alternative commercial outlet for their production [99].

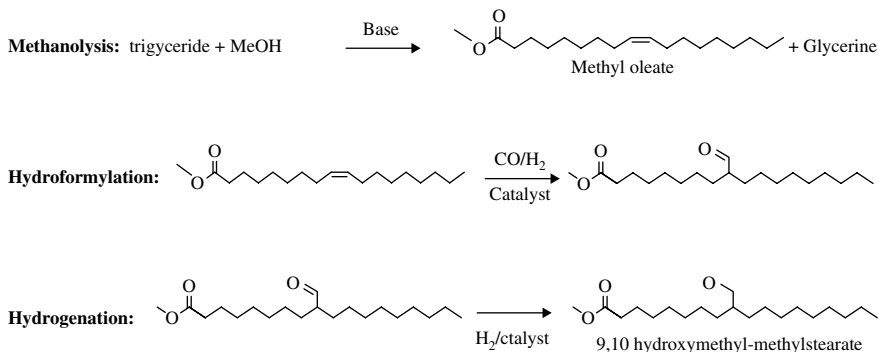


FIGURE 2.43 Procedure for formation of polymerizable ester alcohols from seed oil triglycerides by a hydroformylation and reduction procedure. From Ref. [100]. © Elsevier.

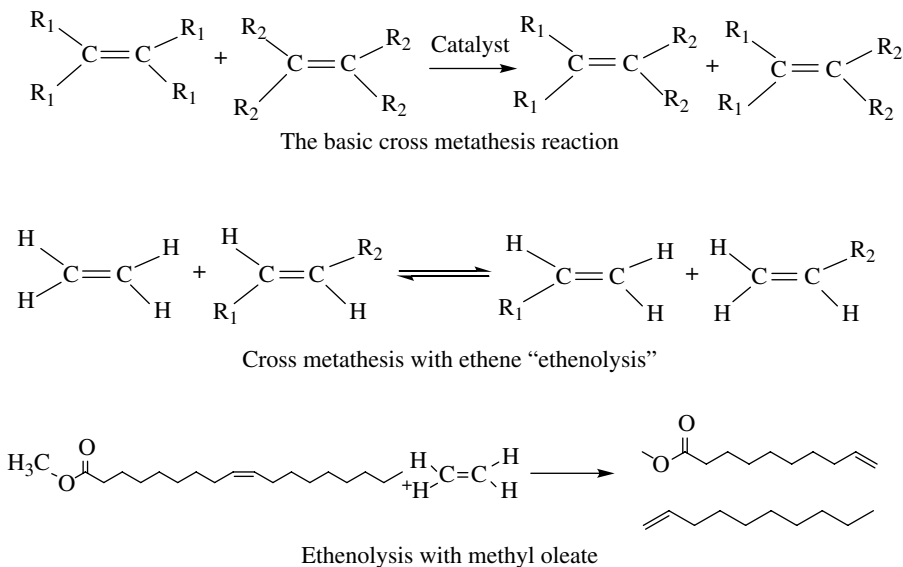


FIGURE 2.44 Illustrative procedure of olefin metathesis reactions and metathesis applied to the ethenolysis of oleic acid.

Metathesis Metathesis is an organic reaction that enables the redistribution of olefin bonds through a scission and recombination mechanism. In the context of seed oil modification for the purpose of creating urethane capable feedstocks, this modification creates useable products for urethane and polyolefin applications [102, 103]. A pictorial image of the action of cross-metathesis exchange envisioned useful in this context is shown in Figure 2.44.

The product ester olefin can be then be readily functionalized to a terminal ester alcohol A–B monomer for polymerization by hydroformylation and reduction as

described in Section “Hydroformylation and Reduction”. The alpha olefin shown can be directly incorporated into polyolefin polymerizations.

New catalysts for metathesis have improved their compatibility with modern industrial processes. The commercialization of these catalysts has resulted in products from metathesis becoming available commercially [104]. Obstacles to fully realizing a large-scale application of this technology are similar to those of the hydroformylation and reduction technology described in Section “Hydroformylation and Reduction” associated with separations and the cost of chemical production requiring large numbers of unit operations.

2.1.6 Prepolymers

The term “prepolymer” can be misleading to someone not fully conversant in the patois of polyurethane terminology. A polyurethane prepolymer is one in which all of the polyol hydroxyl end groups have been reacted with isocyanate groups leaving isocyanate functionality at the termini instead of hydroxyls. In principle, a prepolymer molecular weight should be the molecular weight of the polyol plus two times the molecular weight of the diisocyanate capping the polyol. In practice, things are rarely that neat [105]. Figure 2.45 shows a simplified view of the reactants to products of prepolymer production.

In principle, a prepolymer could be formed by reacting diisocyanates with an excess of polyol to produce a polyol functional prepolymer with urethane functionality at its center, but this is not practiced commercially and the term “prepolymer” is always used to refer to polyols terminated with isocyanate functionality. The excess isocyanate is required to prevent molecular weight growth caused by opportunistic chain extension of unreacted polyol reacting with the isocyanate-terminated prepolymer. In practice, chain extension always occurs but can be limited by increasing the ratio of isocyanate to hydroxyl functionality. A true “prepolymer” in this regard would then distill the excess isocyanate from the product. In the case where the excess isocyanate is left in the product, this is referred to as a “quasi-prepolymer” [106]. In practice, quasi-prepolymer refers to systems with relatively high levels of free isocyanate (>12%), while prepolymer refers to systems with low levels of free isocyanates (<12%). Overall, over 400 million pounds a year of prepolymer is used commercially for many applications where the advantages of prepolymers can be realized.

Prepolymers find application for several reasons. Among the advantages are that there is improved handling since prepolymers are liquids, they are storage stable (when kept dry), and they provide a source of isocyanate functionality with lower vapor pressure than free isocyanates. Additionally, a prepolymer will usually provide better compatibility between additional polyurethane formulation components since the reacted systems provide lower surface tension to other chemicals within the solubility parameter range. Lastly, it is believed that the prepolymer allows one to “prebuild in” the final polymer properties and obtain a more uniform final polyurethane structure [107, 108]. This is particularly true in cast urethane systems where mixing and physiochemical polymer kinetics are more limited and make obtaining equilibrium-phase structures more difficult (see Chapter 9).

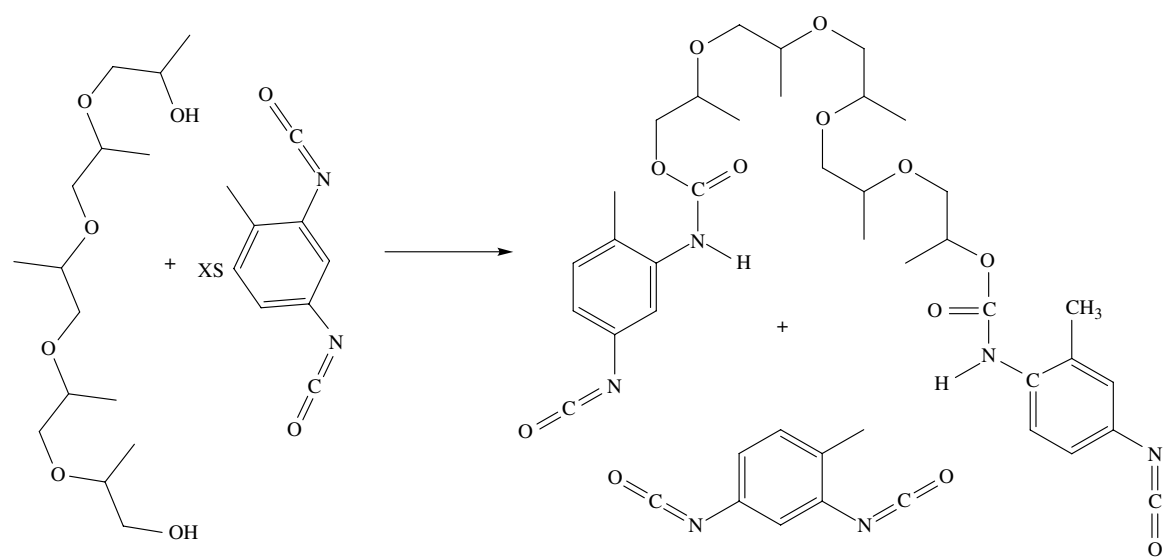


FIGURE 2.45 General preparation of a TDI—polypropylene oxide prepolymer.

As a practical consideration, prepolymers are usually used and defined on the basis of their percent isocyanate or more commonly as “percent NCO.” On reflection, the calculation of this parameter is not as intuitively defined as desirable and so merits exposition. The definition of %NCO is by equation

$$\frac{\% \text{NCO}}{100} = \frac{(42/Y) \times Y}{X + Y + Z} \quad (2.10)$$

where Y = the equivalent weight of the isocyanate, X = equivalent weight of the polyol, the weight of NCO = 42, and $X + Z$ = the number of grams of isocyanate that must be reacted with Y grams of polyol to make a $N/100\%$ NCO prepolymer or

$$Z = \frac{X + Y}{(42 / (N \times Y)) - 1} \quad (2.11)$$

As an example, if it is desired to prepare a 12.5% NCO prepolymer with methylene bisphenyl diisocyanate (MDI) (equivalent weight = 125 g/NCO eq) with a polyol having equivalent weight = 1633 g/eq; using the equation for Z , one would need

$$\frac{1633 + 125}{(42 / (0.125 \times 125)) - 1} = 1041 \quad (2.12)$$

Thus, $N + Z = 125 + 1041 = 1166$ g of isocyanate per 1633 g of polyol (total mass of 2799 g) to make the desired 12.5% NCO. Smaller quantities would be prepared by a simple ratio adjustment.

Prepolymers offer an attractive approach allowing one to prepare cast systems, especially elastomers, from entirely liquid components. Using pure MDI, for instance, would require that all ingredients be heated to a temperature greater than the MDI melting point (ca. 55 °C), which could shorten the window for convenient processing considerably. As a liquid, it is additionally convenient to begin with a system that is as low viscosity as possible to avoid problems such as entrainment of air during processing. Minimization of viscosity is usually a function of pH control, which under basic conditions can result in trimerization of the isocyanate. Other viscosity-building cross-linking reactions occur in making prepolymers such as formation of allophanates and biurets that are more prevalent in NCO-rich environments.

2.2 ISOCYANATES

Isocyanates, especially polyisocyanates, are highly identified with polyurethane chemistry. While isocyanates are capable of undergoing many reactions, their significance is usually in the context of their relationship to polyurethane polymerization and structure. Isocyanates represent a class of chemicals that are characterized by high reactivity and versatility. This combination of positive attributes has contributed

greatly to the broad application of polyurethane materials but is part and parcel of the complications associated with isocyanates [109]. The most chemically relevant attribute of isocyanate chemistry is its reactivity with molecules having active hydrogens. Such active hydrogens are typically found on molecules having alcohol and amine functionalities and also water [37]. The basic isocyanate structure is given in Figure 2.46.

Since addition polymerization requires that monomers be able to propagate a chain by undergoing multiple reactions, polymerizable isocyanate monomers have at least two isocyanate functionalities. The growth of polyurethane technology has been associated with the ability to produce polymerizable isocyanate monomers at low cost. The low-cost requirement has driven the chemistry to employ available and low-cost building blocks, and industrial production has been optimized to an exceptional extent. The two highest volume isocyanates are based in one case on toluene to make toluene diisocyanate (commonly referred to as TDI) and in the other case aniline and formaldehyde to make methylenebis (phenyl isocyanate) (commonly referred to as MDI). The preparation of each of these important molecules and their characteristics will be handled separately. Polyurethanes also function in any number of applications requiring good weatherability. Good weatherability can be hindered by aromatic ring structures, and entirely aliphatic polyisocyanates have been developed for these uses and they will be handled as a class in this chapter.

As discussed in greater detail in Chapter 3, the utility of isocyanates is a result of their electronic structure. As illustrated in Figure 2.47, the unique $N=C=O$ triad results in an electrophilic carbon and a relatively nucleophilic nitrogen [110]. Without going into detail here, this creates an advantageous condition for addition of active hydrogen molecules and formation of urethanes, ureas, allophanates, biurets, and other structures.

The benefits of this seemingly simple reaction have resulted in an industry representing the sixth most common plastic material produced [111]. Much of this is owed to the ability to produce isocyanates from low-cost feedstocks using procedures that

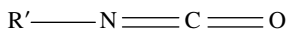


FIGURE 2.46 The isocyanate function.

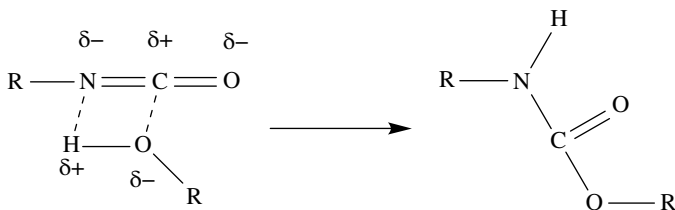


FIGURE 2.47 Assembling the reactants into a transition state geometry for urethane formation.

even if complex could be optimized to an extent that cost is not a barrier to use. As will be discussed at length in the following, the ability to produce isocyanates with attractive economics is because the pathways to product are well established. The result of this is that many isocyanates can be imagined and have been produced using these processes. Regardless, 90% of all isocyanates produced are based on aromatic feedstocks, and of these, there are only two substrates for polyisocyanates: one beginning with toluene and the other beginning with aniline [112]. From these substrates are produced TDI and MDI (or pMDI). The other 10% of isocyanate volume is based on one of several aliphatic substrates [113].

As commodity chemicals, the isocyanate segment of the polyurethane industry is closely associated with the equilibrium between industrial capacity and consumption [114]. Unlike the polyols market of which there are many varieties and continuous innovation based on structure, the isocyanates market is reasonably defined by the TDI and MDI markets and their component feedstocks. Figure 2.48 describes 2011 estimates for the balance between isocyanate industrial capacity to produce and industrial consumption. The ratio of consumption to capacity was about ca. 0.8, suggesting a significant amount of overcapacity in world markets. To an extent, this reflects the downturn in western construction markets and overbuilding of capacity in some developing economies that occurred prior to the economic downturn of 2008. Significant capacity increases in the Middle East are planned under the premise of future economic growth and adoption of rising living standards requiring polyurethane products. The expected annual growth rate is 4.6% for TDI, 5.2% for MDI, and 4.0 for aliphatic isocyanates. The reasons for these disparate growth rates reflect the differing growth rates for the underlying applications and increasing industrial preference for MDI and its preferred occupational health and safety profile.

2.2.1 TDI

TDI is an important industrial chemical because of its central role in polyurethane chemistry. Global production volumes for TDI were 2.6 billion pounds in 1990, 4 billion pounds in 2008, and 4 billion pounds in 2010 and expected to grow to 5 billion pounds in 2013 [115] with an implied growth rate of about 4.5% per year. Demand is driven by the main TDI applications, which are 85% for flexible foams, 10% for coatings, and the remaining 5% spread over numerous small applications. The largest flexible foam applications are furniture, automotive seating, carpet underlay, and mattresses. China was the largest consumer of TDI in 2011 using 30% of available total volume followed by Western Europe using 17%, and then the United States using about 15% [112].

TDI is produced from toluene. As a basic feedstock, it accounts for over 50% of the price of TDI on the market. Interestingly, none of the producers of TDI are back integrated into toluene. The two largest toluene producers are Exxon and Formosa Chemical and Fiber Corporation accounting for about 9% of the total. The toluene market is not concentrated—the top 25 producers only accounting for about 45% of the total produced [116]. Toluene is produced from fuel stocks, and the level of supplier diversity and implied competition accounts for the lack of interest by TDI

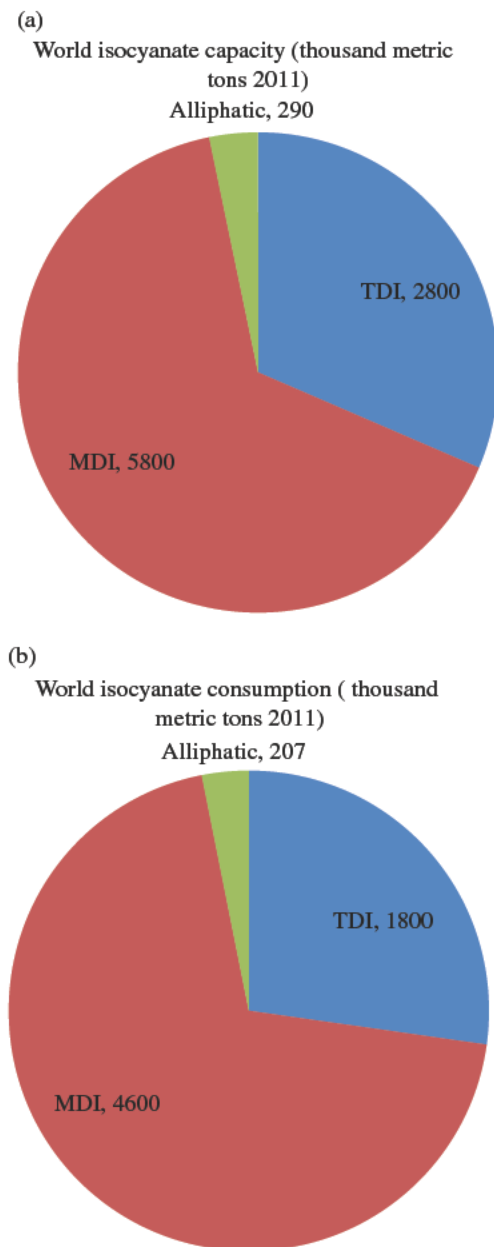


FIGURE 2.48 World (a) capacities and (b) production of isocyanates for polyurethane polymerization [112].

producers to back integrate to toluene. TDI production accounts for only about 5% of toluene consumption; however, as feedstock for chemical synthesis, it is the second largest consumer of value added to toluene (the largest being conversion to benzene/xylenes) (Fig. 2.49).

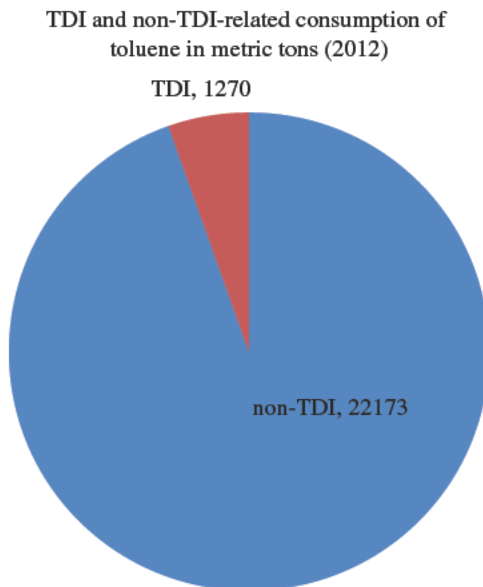
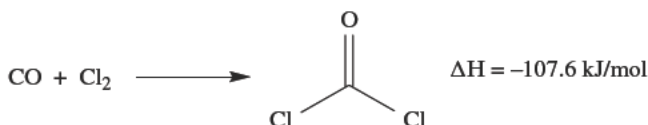


FIGURE 2.49 World toluene production and portion used for manufacturing TDI [116].

Another key component to making TDI and isocyanates, in general, is phosgene. It is produced by the vapor-phase reaction of carbon monoxide with chlorine. The reaction is exothermic and requires cooling to prevent the reversion of phosgene back to reactants above 200 °C:



Due to severe health and safety issues associated with exposure to phosgene, this product is almost never shipped and almost always produced in the plant where its use will occur. A significant amount of engineering optimization is expended on securing phosgene from loss of containment.

2.2.1.1 Conventional Production of TDI A simplified block diagram for production of TDI is given in Figure 2.50. Most TDI produced in the world is from a three-step process as shown. It begins with nitration of toluene, which is subsequently hydrogenated to the polyamine. The last step is reaction of the amine with phosgene to make TDI. Innovations have centered on increasing unit efficiency/reduction of waste and minimization of process phosgene [117–119]. Additionally, there has been ongoing research into nonphosgene routes to polyisocyanates [120]. In Figure 2.50, blocks associated with waste treatment, intermediate purification steps, hydrogen generation, solvent handling, and handling of bottoms products are not included. The

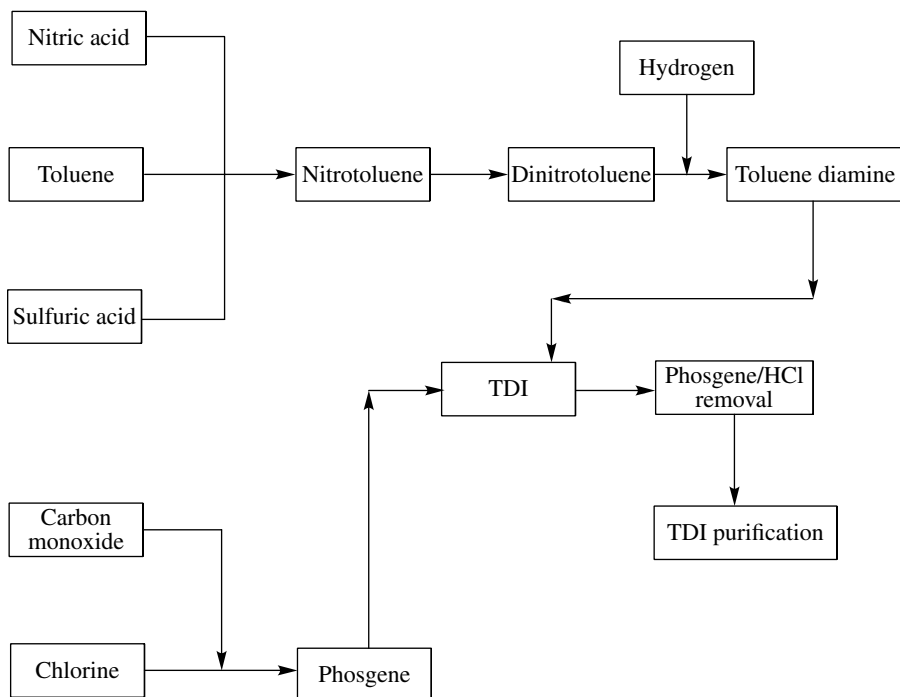


FIGURE 2.50 Simplified block diagram for TDI production.

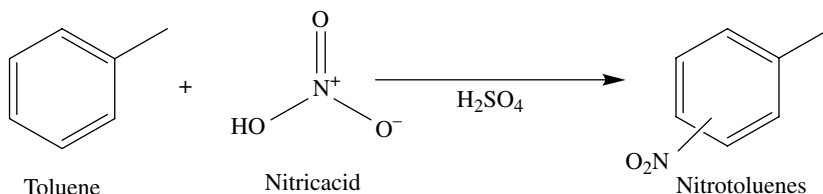


FIGURE 2.51 Preparation of nitrotoluenes from toluene and nitric acid with a sulfuric acid catalyst. Reprinted with permission from Ref. [37]. © John Wiley & Sons, Inc.

first step of the process is nitration of toluene (Fig. 2.51). This simple reaction vastly understates the complexity of pathways leading from reactants to products. Several by-products are formed including cresol derivatives.

In practice, and as shown in the block diagram, nitration is handled in two steps. Formation of the mononitrotoluene is performed with recycled acids from previous production batches at approximately a 30/55 (wt/wt%) ratio. Along with enhancing overall reagent efficiency, it has the secondary effect of reducing nitric acid in the sulfuric acid prior to sulfuric acid regeneration steps. Formation of dinitrotoluene is performed with nearly the same acid concentrations but at higher temperatures. The yield of the desired 2,4- and 2,6-dinitro positional isomers is approximately 96% and about 4% in other isomers. Controls against formation of trinitro isomers are provided

by careful control of acid concentrations and nitration conditions [121]. Figure 2.52 provides explicit pathways of mono- and dinitrotoluene formation. The initial mononitration products consist of 57.5% ortho (substitutes at the 2-position), 38.5% para (substitution at the 4-position), and about 4% meta (substitution at the 3-position). Sulfuric acid is regenerated by removal of water with hot air stripping [122].

The production of nitrotoluenes that avoids use of sulfuric acid and also the expensive sulfuric acid regeneration step has been reported, but is not yet implemented commercially. Problems with the “single acid” nitric acid-only process include creation of more unwanted by-products, slower rates, difficulty in nitrotoluene recovery due to solubility of the product in nitric acid, and an expensive nitric acid regeneration procedure [123].

The second step to production of TDI is hydrogenation of dinitrotoluene to toluene diamine (Fig. 2.53). The hydrogenation is accomplished in a continuous process using a palladium–platinum on carbon or other metal heterogeneous catalyst system [124, 125]. The hydrogenation is thus a multiphase system of dinitrotoluene melt, catalyst, and toluene diamines in water and hydrogen gas. Hydrogen pressure can vary from ca. 100 psig to over 500 psig. The hydrogenation process is exothermic and temperature is carefully controlled (ca 120 °C). Water and orthoisomers are removed by distillation. As with nitration, the mechanism of hydrogenation to the

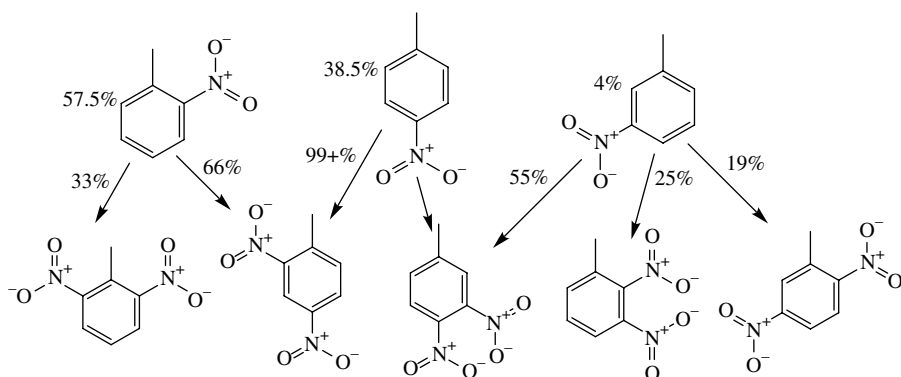


FIGURE 2.52 Pathways and product distributions of dinitrotoluene from mononitrotoluene. Reprinted with permission from Ref. [37]. © John Wiley & Sons, Inc.

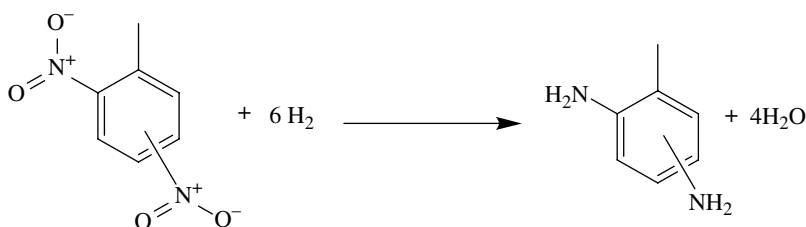


FIGURE 2.53 Preparation of toluenediamines from nitrotoluenes by catalytic hydrogenation. Reprinted with permission from Ref. [37]. © John Wiley & Sons, Inc.

polyamines is very complex, going potentially through hydroxylamine, azo, and hydrazine intermediates among several others.

The third and final step (apart from distillation) is phosgenation of the toluene diamine isomers to diisocyanates (Fig. 2.54).

It is generally accepted that the reaction to isocyanate is a two-step process. First, phosgene reacts with the diamine to form a dicarbamoyl chloride (Fig. 2.55). The dicarbamoyl chloride is not isolated and is directly converted to diisocyanates at elevated temperature (Fig. 2.56) [126].

In a conventional batch process, TDA is dissolved in monochlorobenzene and mixed with liquid phosgene. The mixture is heated to effect reaction, and HCl and excess phosgene are purged with nitrogen. The amine and HCl form an acid–base pair (sometimes referred to as “slurry”), which must be thermally broken, and operationally requires excess phosgene for efficiency. In a continuous process, the carbamoyl chloride is formed at ambient conditions and then pumped to a reaction vessel maintained at an elevated temperature (65–80°C) to form the diisocyanates [127]. A so-called hot phosgenation will gradually increase temperature until there is no more HCl evolved at which point the reaction is considered complete. The hot process has been

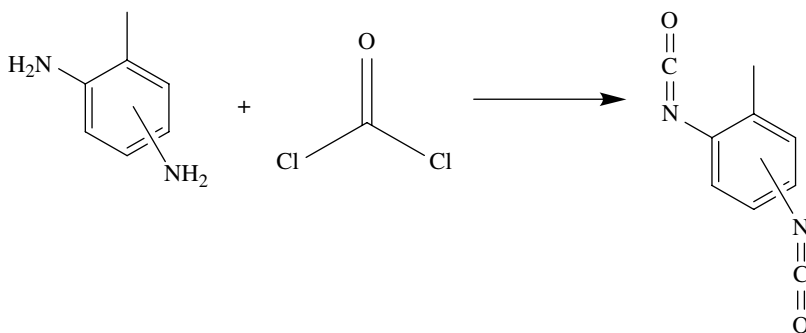


FIGURE 2.54 Phosgenation of toluene diamines to produce toluene diisocyanates. Reprinted with permission from Ref. [37]. © John Wiley & Sons, Inc.

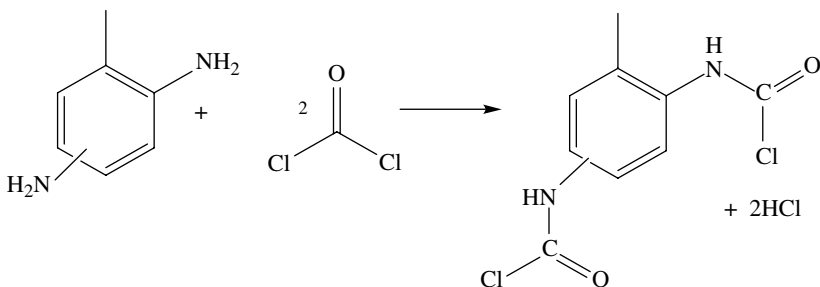


FIGURE 2.55 First step of the phosgenation process forming the dicarbamoyl chloride. The acid product can complex the free toluene diamine requiring application of excess phosgene and heat to complete the reaction.

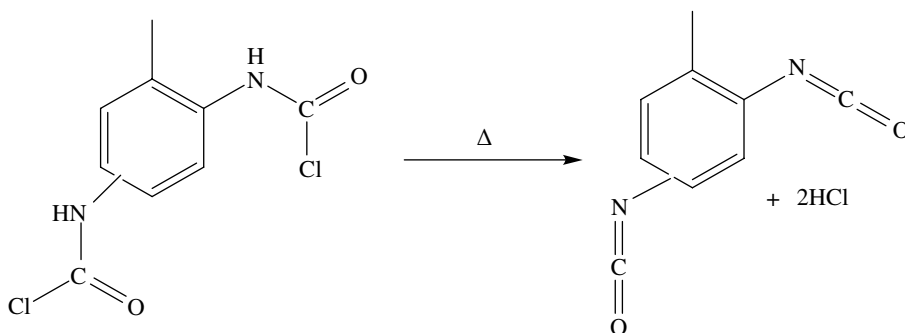


FIGURE 2.56 Thermolysis of the dicarbamoyl chloride to form the isocyanate and acid co-product. The acid is recovered by distillation.

run up to nearly 90% conversion efficiency of toluene diamine to TDI. Unreacted diamine can be recycled back to the phosgenation step, and partially converted isocyanate can be reverted back to the diamine by hydrolysis and sent back for further phosgenation. Reactions of diisocyanates with amines occurring under concentrated conditions, such as urea, biuret, and carbodiimide formation, are additional routes for loss of final product. These reactions will be covered in detail in Chapter 3.

A significant innovation that has developed commercial reality has been the gas-phase phosgenation process originally developed by Bayer and described in a series of patents [118, 128]. The main innovation allows for the efficient formation of diisocyanates without the need for solvent such as monochlorobenzene. This may not sound to the ear like a major breakthrough, but production of commodity chemicals is a very conservative endeavor, especially when there are toxic reagents involved. Although the gas-phase process does incorporate some monochlorobenzene solvent in the phosgenation, the significant reduction reduces the need for handling, heating, and recovering solvents representing savings in capital as well as process expense. Furthermore, the shorter contact time of toluene diamine with phosgene results in a reduction of phosgene inventory required to operate the plant reliably—a considerable health and safety outcome.

In gas-phase phosgenation, TDA, phosgene, and a small amount of chlorinated benzene solvent are heated to very high temperatures ($>300^\circ\text{C}$). The amine and phosgene feeds are mixed in a reactor tube in a manner that maximizes intermolecular interaction [129]. The molar ratio of phosgene to toluene diamine is high to maintain a high reaction rate reflecting second-order reaction kinetics. Residence times and process are optimized for decomposition of the carbamoyl chloride intermediate resulting in yields on the order of 99% of that expected from theory. Solvent, unreacted phosgene, HCl, and by-products are separated as a vapor phase and subsequently quenched and separated for recycle or disposal.

The attractive features of this process are resulting in several announcements of new TDI plant construction based on the gas-phase phosgenation technology and perhaps have contributed to closing of older less profitable assets by other companies. The economic advantage in cost of manufacture using gas-phase technology for a large (660 million pound/year) TDI plant is on the order of 10%—a large difference for commodity chemicals [130].

2.2.1.2 Nonphosgene Routes to TDI Gas-phase phosgenation technology described in Section 2.2.1.1 results in industrial efficiency including reduced use of phosgene. Other pathways of TDI production have been explored to forgo phosgene consumption altogether. While these processes are in no way economically competitive with conventional phosgenation and even less so with gas-phase phosgenation (disadvantaged by about 25 and 35%, respectively), these costs do not reflect the incalculable potential costs associated with a phosgene accident. Three nonphosgene routes to TDI will be covered in the following. The first two have in common that isocyanate functionality is produced by making urethane and then thermally decomposing the urethane to isocyanate and alcohols. The differences are in how the initial urethane is achieved. The last, based on the Curtius reaction, is made by decomposition of an intermediate azide.

Thermolysis of Carbamic Acid, N,N' -(4-Methyl-1,3-Phenylene)Bis-, C,C' -Dimethyl Ester Made from the Reaction of Toluene Diamine with Methyl Carbonate The reaction of toluene diamine with DMC is known to produce the diurethane of TDI (Fig. 2.57) [131]. DMC is a commodity chemical prepared from the oxidative carbonylation of methanol [132]. The reaction proceeds via progressive heating of DMC and the toluene diamine up to about 170 °C. The diurethane product is subsequently heated to produce the diisocyanates and methanol, which is removed and recycled back to form DMC (Fig. 2.58). Yields of TDI are 90% based on input toluene diamine.

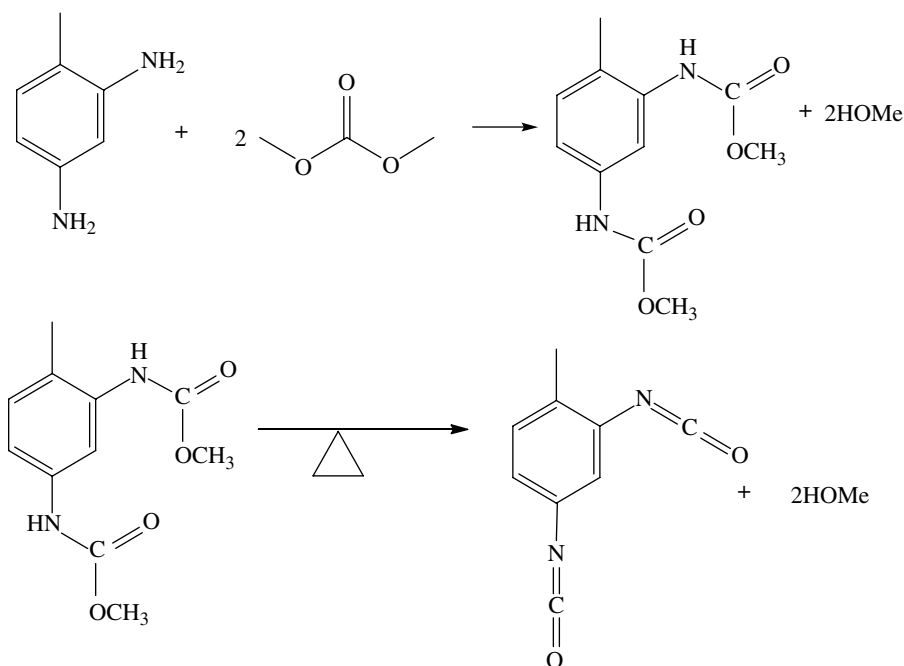


FIGURE 2.57 Preparation of TDI by reaction of toluene diamines with dimethyl carbonate followed by thermolysis to the diisocyanates.

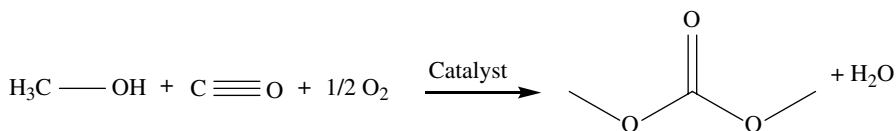


FIGURE 2.58 Preparation of dimethyl carbonate.

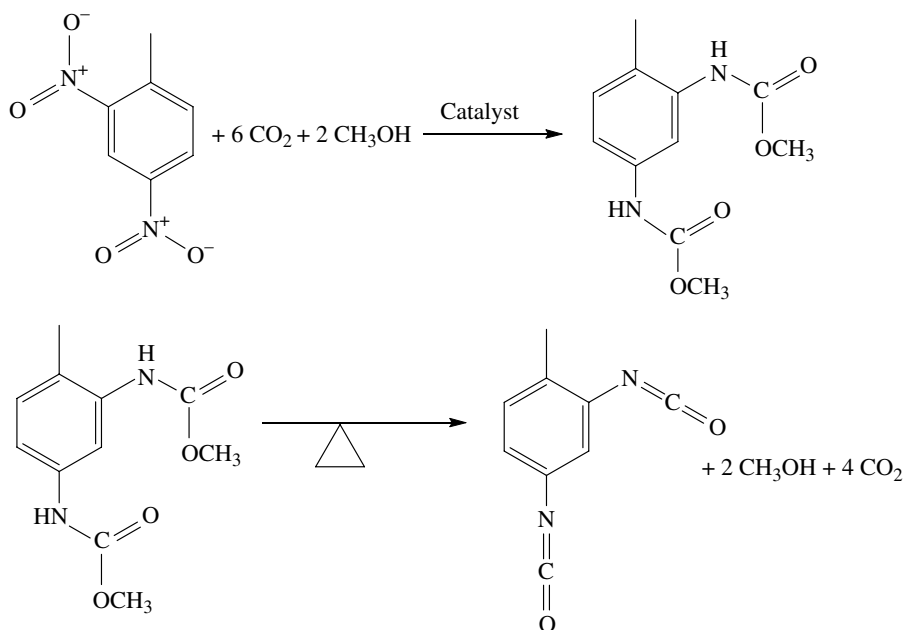


FIGURE 2.59 Process for reductive carbonylation for non-phosgene production of TDI. Reprinted with permission from Ref. [37]. © John Wiley & Sons, Inc.

Thermolysis of Carbamic Acid, N,N'-(4-Methyl-1,3-Phenylene)Bis-, C,C'-Dimethyl Ester Made from the Reductive Carbonylation of Dinitrotoluene Catalytic reductive decarbonylation of aromatic nitro compounds to isocyanates has been known since 1967 [133]. Demonstration of this reaction stimulated a significant amount of research on catalysts and cocatalysts to provide ever greater activity and selectivity. It eventually became apparent that while conversion of dinitrotoluene to TDI could occur, it could not occur with sufficient efficiency to provide a commercial process. It was later observed [134] that with a $[\text{Pd}(\text{OAc})_2, 1,10\text{-phenanthroline}]$ catalyst, exceptionally efficient carbonylation of dinitrotoluene to dicarbamate could be effected in an alcohol solvent. The formation of the carbamate can be conceptualized as the formation of the isocyanate and subsequent stabilization via reaction with the alcohol solvent (Fig. 2.59). This concept has been validated by observation of urea formation when the reaction occurs in the presence of amine. The mechanism for such a large and complex transformation is clearly a matter of debate. One simplified

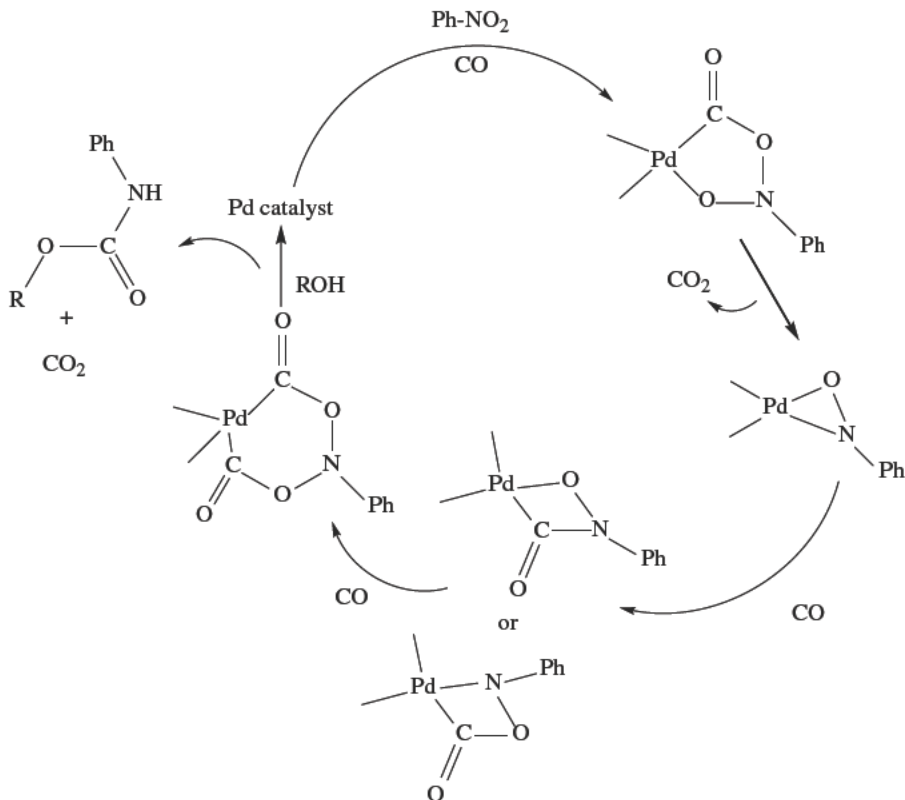


FIGURE 2.60 Simplified proposed mechanism for Pd catalyzed reductive carbonylation to carbamate product [137].

mechanism involves stepwise catalyst coordination, followed by insertion and elimination reactions, ending in the final carbamate product (Fig. 2.60) [135, 136]. Less expensive selenium catalysts have also demonstrated high conversion to carbamate. After the carbamate is formed, thermolysis is achieved at about 260°C with methanol removed overhead. Despite high levels of optimization, this route has not achieved sufficient efficiency to make a viable industrial process.

Isocyanates by Thermal Decomposition of Acyl Azides: The Curtius Rearrangement

Carboxylic acid chlorides can be converted to isocyanates via prior formation of the carbonyl chloride [138]. The azide can be prepared by initial reaction of the acid chloride with a reagent such as sodium azide or by reaction of the acid hydrazide with nitrous acid. The azide can be converted to isocyanate by heating to about 100°C (Fig. 2.61) [139]. This reaction has been demonstrated using aliphatic, alicyclic, aromatic, and heterocyclic compounds. The explosion hazards of handling and heating azides makes this reaction unworkable from a practical perspective.

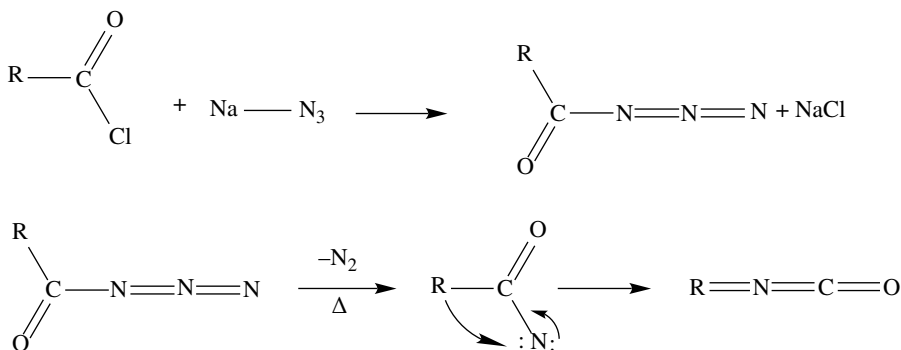


FIGURE 2.61 Non-phosgene preparation of isocyanates via the Curtius rearrangement.

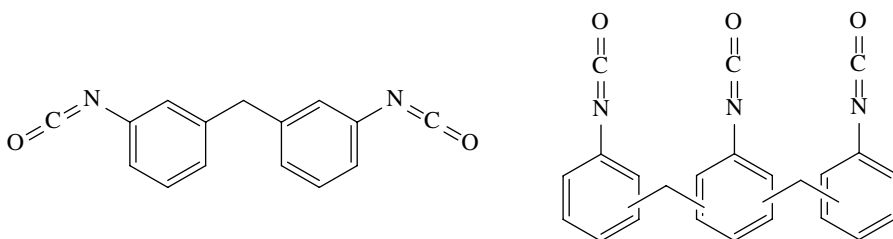


FIGURE 2.62 Illustrative structures of MDI and pMDI. Reprinted with permission from Ref. [37]. © John Wiley & Sons, Inc.

2.2.2 Diphenylmethane Diisocyanates (MDI)

MDI is the largest volume industrial isocyanate produced (Fig. 2.62). Global production of MDI was 4600 thousand metric tons in 2011 and is projected to be nearly 6000 thousand metric tons in 2016 with an implied annual growth rate of about 5%. The largest volume uses for MDI are rigid foams, adhesives, sealants, coatings, elastomers, and flexible polyurethane foam. Rigid foam applications monopolize about 60% of the total MDI volume. Europe supports the largest MDI production capacity (33%) followed by the United States (25%), China (21%), and Japan (10%). It has been estimated that China's growth will encompass MDI capacity growth to about 33% of the world total by 2020, taken approximately evenly from the other regions [112].

MDI is produced from aniline and formaldehyde feedstocks. Aniline is produced sequentially from the nitration of benzene followed by reduction to aniline by hydrogenation (Fig. 2.63). In contrast to TDI being a minor consumer of feedstock toluene (~5%), MDI consumes more than 75% of world aniline production (Fig. 2.64) [140]. Thus, the economics of aniline and MDI production are very tightly correlated and dependent on each other. Furthermore, since most aniline is produced and used captively by MDI producers, MDI manufacturers that are not back integrated to aniline are potentially disadvantaged from a supply and a price perspective. Potential supply constraints are theoretical since capacity consistently exceeds demand and is

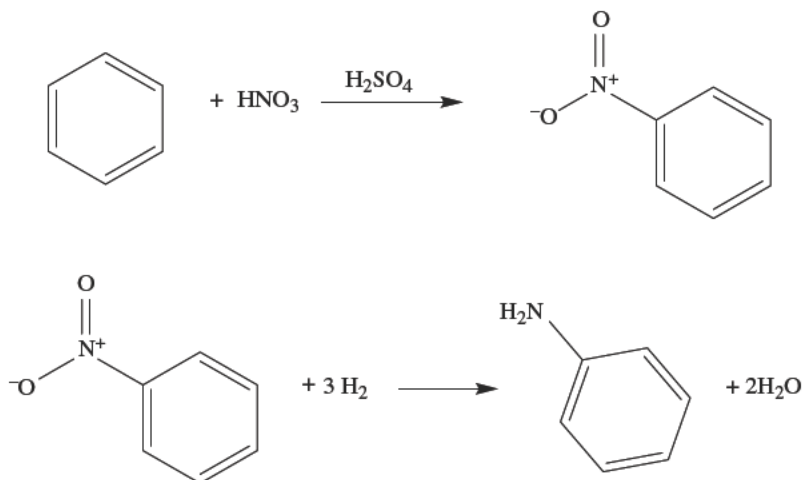


FIGURE 2.63 Nitration of benzene to nitro benzene followed by hydrogenation to aniline—a fundamental feedstock for MDI production.

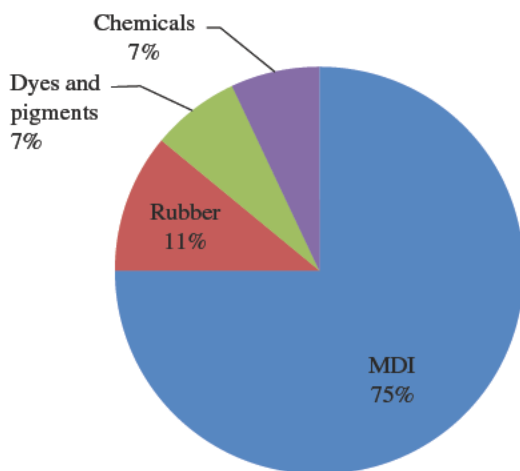


FIGURE 2.64 Global usage of aniline in 2010. The vast majority is used for making MDI which tethers their production and costs to each other.

projected to for the future. However, MDI manufacturers who purchase rather than make MDI may be between 5 and 10% disadvantaged in overall cost of manufacture. As a commodity chemical, the price of MDI cannot be adjusted for a particular manufacturer's cost positions, and so capital savings associated with not manufacturing aniline results in a reduced profit margin. Capacity for MDI production in 2010 was approximately 7200 thousand metric tons, while consumption was 5600 thousand metric tons representing about 78% capacity utilization.

Formaldehyde is another feedstock for MDI production. It is a very important commodity feedstock with many applications, particularly in thermoset polymers such as urea, phenol, and melamine formaldehyde resins used in many applications, particularly in wood bonding. Use in MDI manufacture only accounts for about 5% of total formaldehyde consumption and so is not a major determinant of formaldehyde pricing, but may correlate to MDI demand due to overlap in applications with other uses of formaldehyde such as construction [141]. Made from the catalytic oxidation of methanol, Bayer and BASF produce some formaldehyde for captive production of MDI, but most formaldehyde for MDI production is purchased from companies outside of the polyurethane industry.

2.2.2.1 Production of MDI A simplified block diagram for production of MDI is shown in Figure 2.65. There are many similarities to production of TDI with the essential steps of (i) nitration, (ii) reduction, and (iii) phosgenation being the same. Structurally, the fusing of the aromatic rings by formaldehyde condensation particularly stands out as a difference and has a pronounced effect on eventual urethane properties and optimal applications [142]. The condensation chemistry also produces isocyanate oligomers. The oligomers of MDI actually have more commercial use than the monomer and make it very difficult to treat MDI as a single entity as generally is the case with TDI. Industrially, 1 kg of MDI is produced from 0.8 kg of aniline and 0.9 kg of phosgene producing 0.6 kg of waste HCl.

Innovations in MDI process technology center on incremental improvement in product recovery, reagent minimization, distillation versus crystallization of MDI monomer, plant debottlenecking, etc. Heterogeneous catalysis rather than homogeneous acid catalysis would remove the need for handling caustic for reaction neutralization as

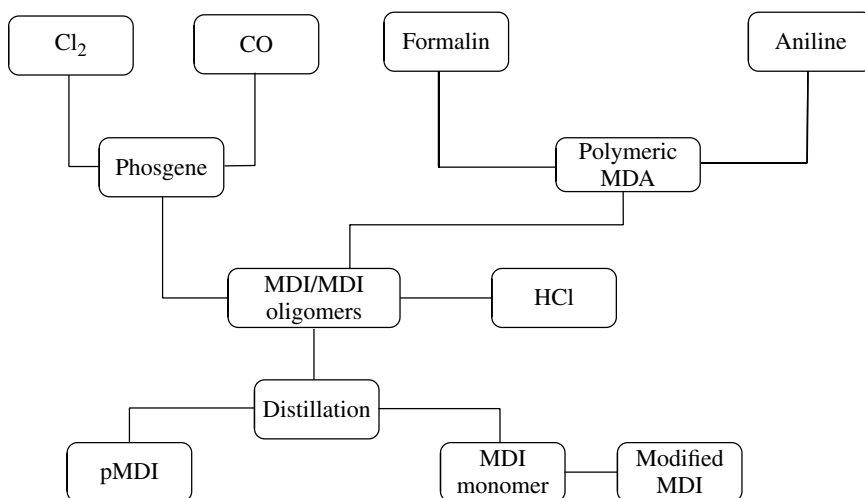


FIGURE 2.65 Simplified block diagram for production of monomer, polymeric, and modified MDI.

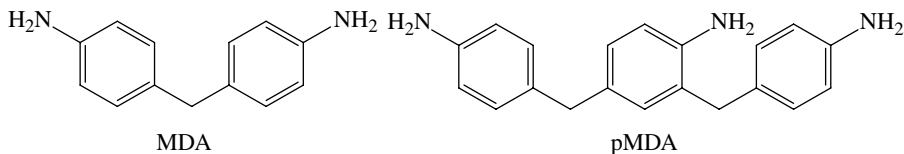


FIGURE 2.66 Structures of 4,4' methylene bisphenyldiamine and the MDA polymer.

well as product salt. Nonphosgene routes have been explored for production of MDI as have been for TDI [143]. As with TDI, there is no forecast of these routes finding economic viability. Potential future changes may be to develop plants that flexibly produce monomer MDI, removing the need for distillation steps and serving the higher value monomer markets. Alternatively, construction of plants that exclusively produce pMDI could be envisioned, again removing the need for product separations and maximizing assets to most economically serve the largest volume markets [37].

The diversity of MDI-based products and the means by which producers distinguish their respective products originate in the reaction of aniline with formaldehyde to form MDA and its oligomers (Fig. 2.66). Details of how this reaction is conducted are tightly controlled process variables and industrial secrets.

The mechanism of acid-catalyzed condensation of aniline and formaldehyde does not lead to a single product, but instead to a mixture of MDA positional isomers and oligomers. Control of the final product distribution depends on process variables such as aniline-to-formaldehyde ratios, reaction temperatures and times, and the acid catalyst employed. Figure 2.67 is a simplified pathway for aniline and formaldehyde to reach the final products [144, 145]. The initial product of reaction is the *N*-methylaniline, which loses water rapidly to form the Schiff base. The Schiff base reacts with adventitious aniline to form aminals—one being linear and the other being cyclic. The relative amounts of these forms depend on the ratio of aniline to formaldehyde. The undesired cyclic form is favored when the aniline-to-formaldehyde ratio is low, while the linear form is favored at aniline-to-formaldehyde ratios greater than 2:1.

As mentioned, there is a cyclic product (Fig. 2.68) that can be formed from the Schiff base that is in principle reversible but in practice is avoided by process control. Furthermore, the products and intermediates after formation of the Schiff base conversion to the aminals are not observed except under acidic conditions. The final step to MDA is not reversible, and the reaction with the carbonium ion intermediate is the basis for modern MDI technology and 75% of commercial volume. It should also be clear that the last step to form MDA is not exclusive to formation of the 4,4' products and that the 2,4 product can form and certain process parameters can hinder or enhance its formation.

Process control can influence the product distributions of these reactions. As alluded earlier, the aniline-to-formaldehyde ratio is an obvious variable. Ratios of aniline to formaldehyde are typically 2–5 with higher MDA monomer yields produced at the higher ratios and MDA oligomer produced at lower ratios [146]. Increasing the acid to aniline ratio is also observed to increase MDA monomer composition in the final product. Higher reaction temperatures result in increased oligomer formation as do increases in reaction time and water content (Table 2.11).

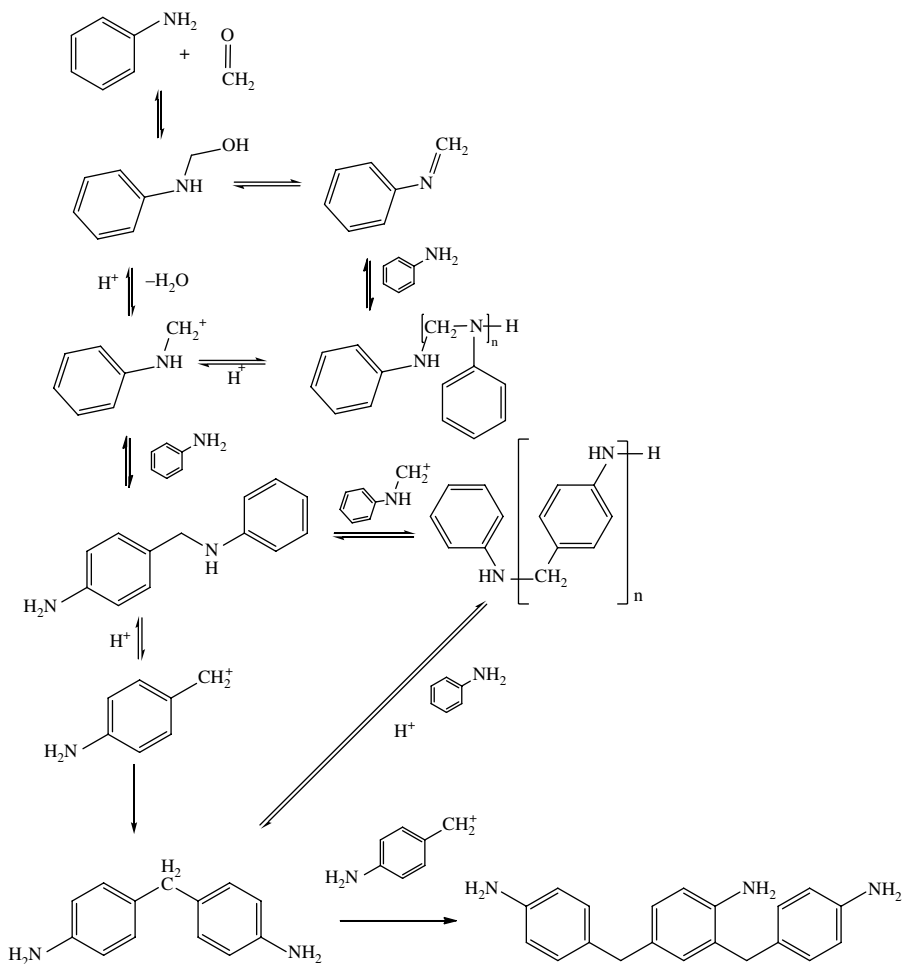


FIGURE 2.67 Mechanism for production of polymeric and monomeric MDA by reaction of aniline and formaldehyde. Product structure and distribution is largely determined in this step.

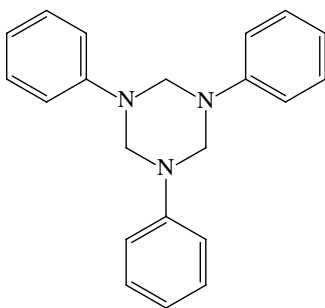
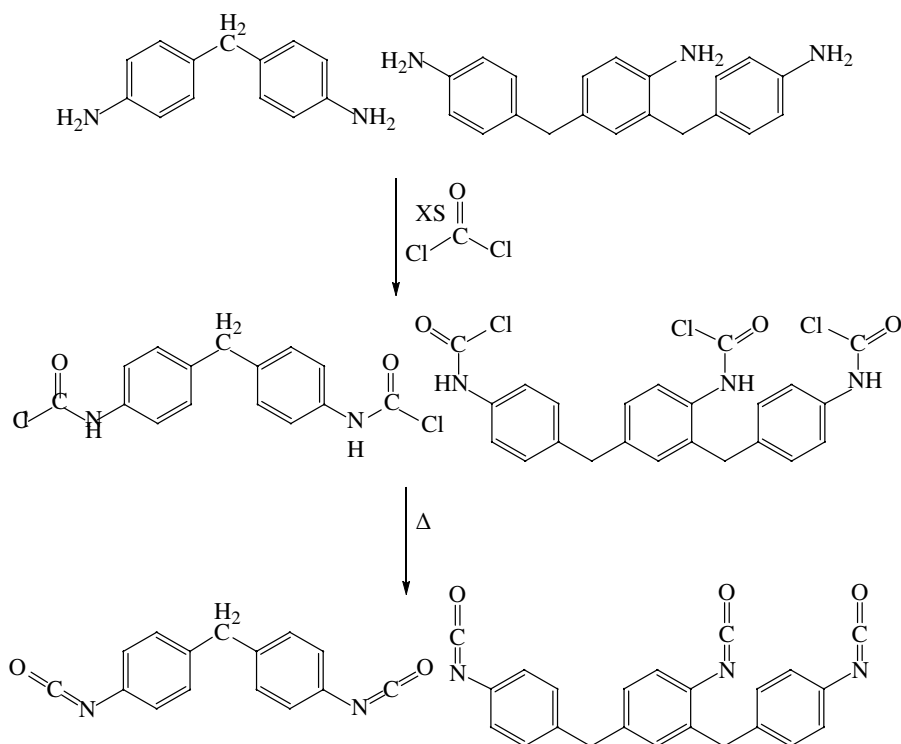


FIGURE 2.68 1,3,5-triphenylhexahydropyrimidine formed by trimerization of the Schiff base intermediate in the production of MDA.

TABLE 2.11 Effect of process variable ratios on relative production of monomeric and polymeric methylene bisphenyldiamine

Process variable	Process direction	MDA	pMDA
Aniline/formaldehyde	Increase	Increase	Decrease
Acid/aniline	Increase	Increase	Decrease
Temperature	Increase	Decrease	Increase
Reaction time	Increase	Decrease	Increase
Water content	Increase	Decrease	Increase

**FIGURE 2.69** Phosgenation of MDA and pMDA to form MDI and pMDI.

The phosgenation of MDA and pMDA mixtures follows a similar pathway to that of TDI. A solution of the aromatic anilides is dissolved in a solvent such as monochlorobenzene and then mixed with liquid phosgene to form the carbamoyl chloride. The carbamoyl chlorides are then heated to drive off HCl , which is stripped along with the excess phosgene for recycle back to the production process (Fig. 2.69) [147]. The efficiency of amine conversion to isocyanate in the phosgenation reaction is quite high. About 0.8 kg of MDA produces about 1 kg of MDI (pMDI). The efficiency of the phosgene reaction does not preclude the formation of unwanted side products, some of which are well known and are

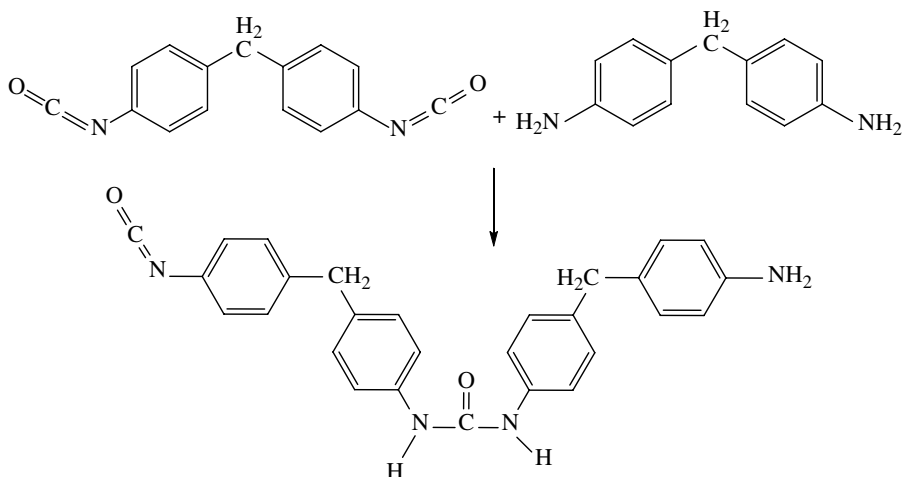


FIGURE 2.70 Side reaction in MDI production between MDA and MDI to form a urea.

quantified in product specifications. One such reaction is the diffusion-limited reaction between amines and the freshly produced isocyanates to form urea functionality (Fig. 2.70). The by-product of Figure 2.70 is of course fully capable of further additional side reactions. Among the reactions the urea by-product can undergo is the phosgene-stimulated hydrolysis of urea to carbodiimide, which can then react with excess isocyanate to form the imino-uretidinedione, which in this context is referred to as “APA” (Fig. 2.71). The addition of another isocyanate to the 4-member ring creates a 6-member triazine ring, another side product of the reaction termed “AP6.”

Parameters associated with phosgenation and control of the final products are given in Table 2.12 [148].

Industrially, a portion of pure 4,4' MDI is usually distilled from the pMDI mixture. Historically, the polyurethane industry has consumed as much of this 4,4' component as can be produced, and controlling production has had the effect of maintaining the price. The applications for 4,4' MDI monomer are elastomers, adhesives, and notably spandex fibers. Another reason for manufacturers to limit production is related to the limited shelf life of the pure 4,4' monomer [149]. In the solid state, the 4,4' monomer undergoes a facile dimerization reaction to form the uretidione (Fig. 2.72) [150]. This reaction is intrinsic to the reactivity of isocyanate functionality and the packing of 4,4' MDI in its crystal state [151]. The maximum in the conversion rate is unfortunately around ambient storage temperatures (Fig. 2.73). This warrants normal laboratory storage in freezer conditions. Industrially, 4,4' MDI is maintained in the molten state to facilitate pumping and minimize dimer formation. Regardless, the monomer does not have a long shelf life and must be used in a relatively short time after production.

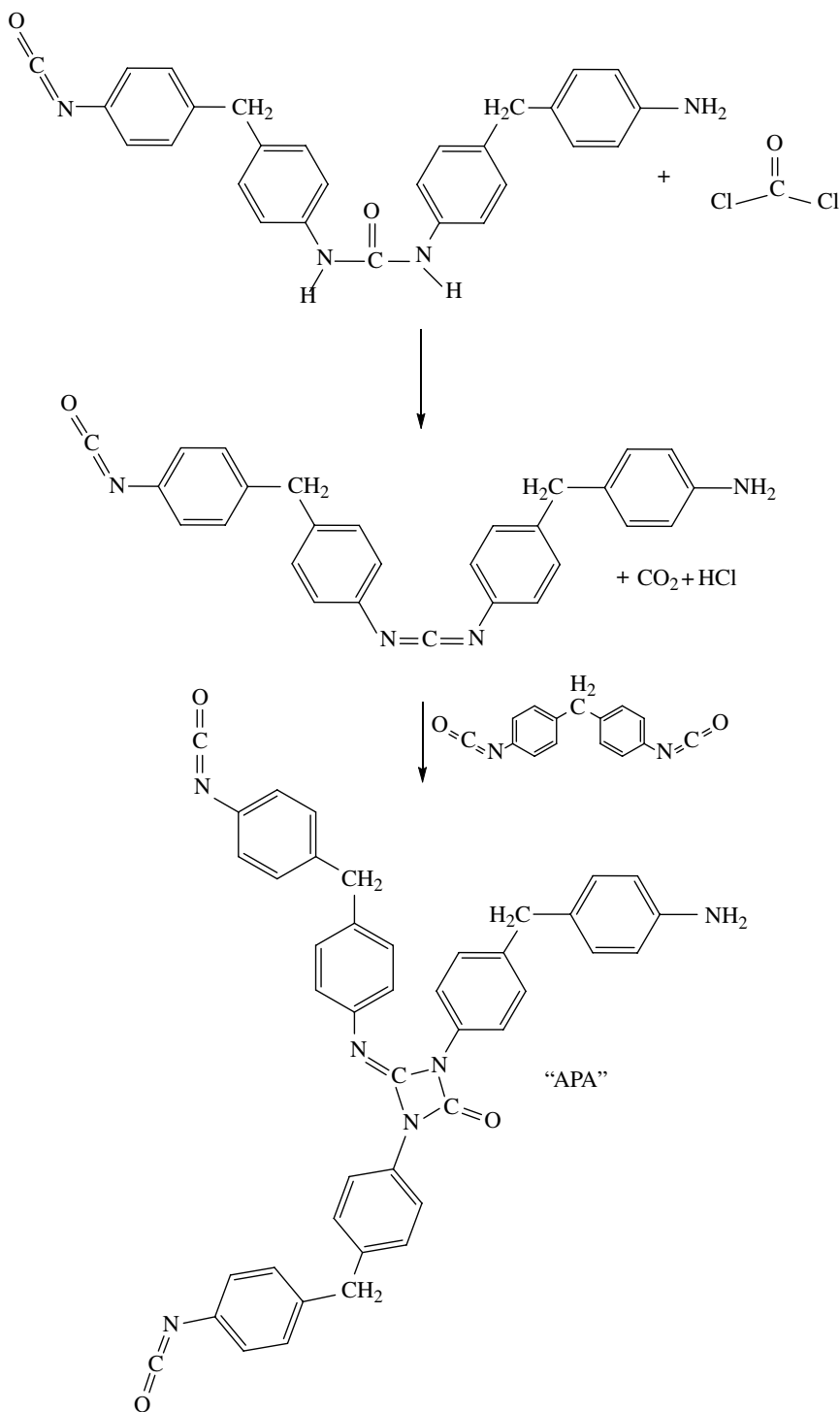
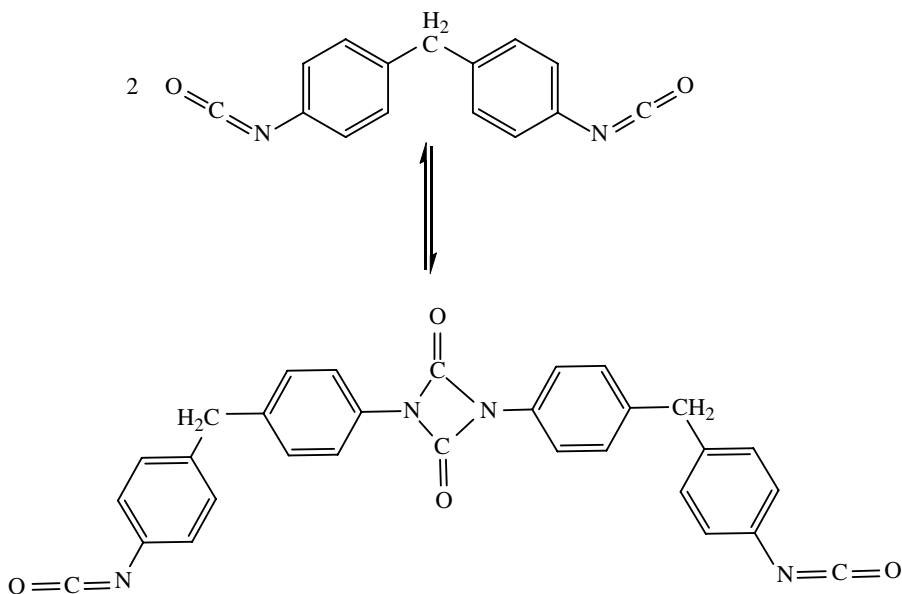


FIGURE 2.71 Formation of APA—a common impurity in pMDI, usually quantified in a producer’s certificate of analysis.

TABLE 2.12 Effect of process variable ratios on the production of desired MDI and PMDI (the “process”) and reactions resulting from numerous potential side reactions

Process parameter	Process direction	Side reactions	Notes
Phosgene/pMDA ratio	Increase	Decrease	Ratio usually 6–8 ~30–35%
Concentration pMDA in solvent	Decrease	Decrease	
Residence time in reactor	Increase	Increase	
Reactor temperatures	Increase	Increase	~200°C

**FIGURE 2.72** Formation of uretidione, a common undesired side reaction resulting from dimerization of the isocyanate reaction. The reversion from the dimer to the monomers can occur at temperatures over 100°C.

2.2.3 Aliphatic Isocyanates

About 500 million pounds of aliphatic isocyanates was consumed in 2011, and the expected growth rate for this industrial segment is between 3 and 4% per annum. The vast majority of aliphatic isocyanates are used for coatings. This application particularly takes advantage of the reduced weather-induced coloring of aliphatic-based urethanes versus aromatic-based polyurethanes (Fig. 2.74). Additionally, a small amount of aliphatic isocyanates is used in thermoplastic polyurethane films that are also used for weatherable applications. About 40% of aliphatic isocyanates are consumed in Asia, about 34% in Europe, and 24% in North America. The growth

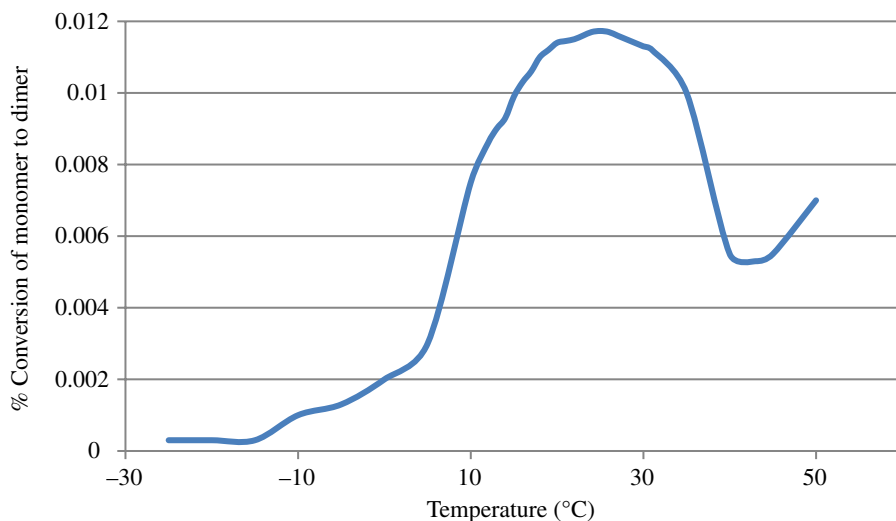


FIGURE 2.73 Measured percentage molar conversion of MDI monomer to dimer *per day* as a function of temperature.

rate is highest in the developing economies, but does not mirror the difference in overall economic growth with growth somewhat slower than expected on macroeconomics [112]. Aliphatic isocyanates are typically characterized in contrast to aromatic isocyanates by their superior weatherability, by their relatively slow reactivity, and by their being substantially more expensive.

Three aliphatic isocyanates represent more than 95% of the total aliphatic isocyanate world production. They are in order of size hexamethylene diisocyanate (HDI), isophorone diisocyanate (IPDI), and the hydrogenated version of MDI, 4,4'-diisocyanatodicyclohexylmethane (H_{12} MDI). Approximately half of the total used is HDI, 30% is IPDI, and the rest is H_{12} MDI. Almost 90% of aliphatic isocyanates are used in coatings and 6% in elastomers. Almost half of the polyurethane coatings that use aliphatic isocyanates are automotive related. The other volumes are spread disparately over many relatively smaller applications. The structures of the three main isocyanates are shown in Figure 2.75.

The need for aliphatic isocyanates stems from the photooxidative instability of aromatic isocyanate structures. The photooxidative instability mechanisms have been well studied and are, of course, complex [152]. MDI-based urethanes tend to show an increased tendency to yellow upon light exposure. It is believed that this is due to formation of the quinone-diimide product shown in Figure 2.74 [153, 154]. It is also shown that under other circumstances, a photo-Fries-type rearrangement can occur resulting in anilide formation, which is known to oxidize and discolor upon further oxidation (Fig. 2.74). In addition, it has been shown that the soft segment can have a significant influence on photodegradation with increased degradation occurring with increased soft segment flexibility [155].

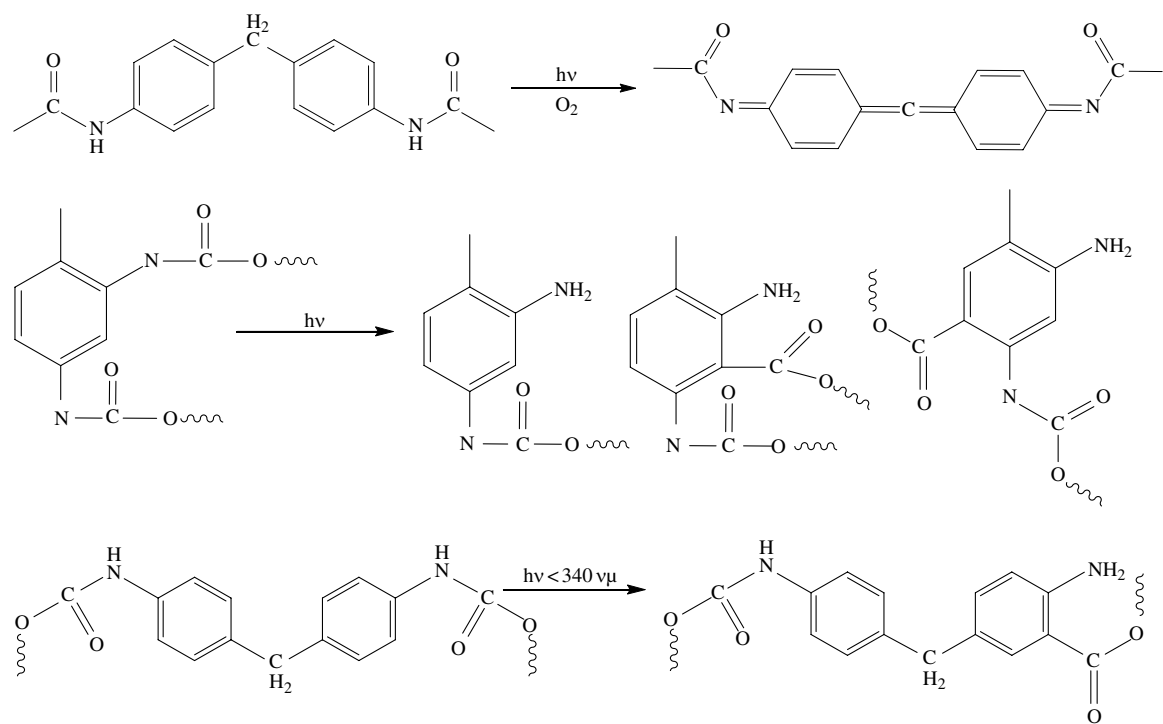


FIGURE 2.74 Oxidation processes of isocyanates leading to color in polymers. The intrinsic nature of these reactions leads to the favored uses of aliphatic isocyanates in weathering applications.

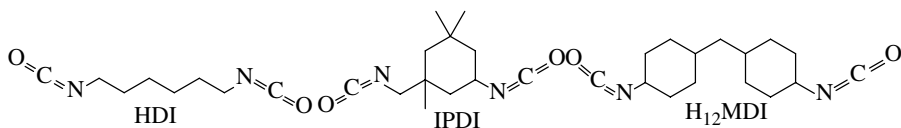


FIGURE 2.75 Structures of common and commercially available aliphatic isocyanates.

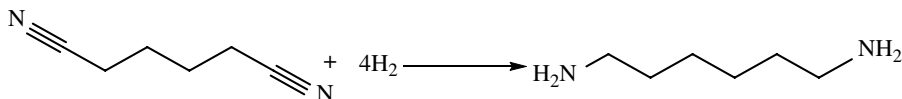


FIGURE 2.76 Process to produce hexamethylenediamine from adiponitrile.

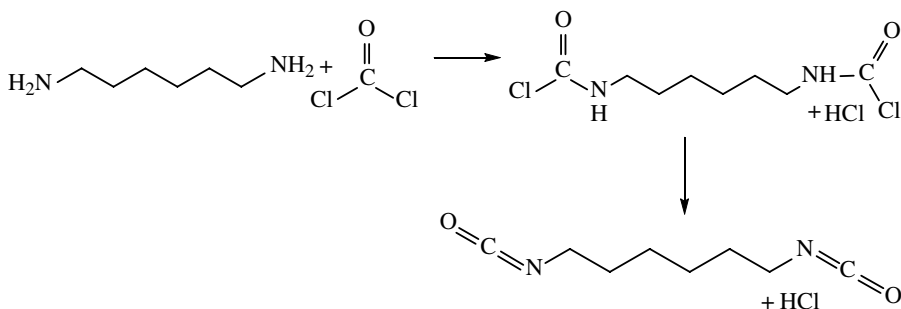


FIGURE 2.77 Phosgenation of hexamethylenediamine to hexane diisocyanates.

2.2.3.1 Production of Aliphatic Isocyanates

HDI The largest volume diisocyanate, HDI, is produced from feedstocks that do not depend on the HDI manufacture for their economic structure. HDI is prepared from the phosgenation of hexane diamine in a manner quite analogous to that of aromatic polyisocyanates. Over 1100 thousand metric tons of hexamethylene diamine was produced in 2010 with an expected annual growth rate of about 2.5%. Most of this volume is prepared for manufacture of nylons (polyamides), and the diamine represents a backward integration into feedstocks [156]. Feedstocks for adiponitrile are butadiene or alternatively acrylonitrile. Once adiponitrile is formed, the diamine is formed by reduction with hydrogen (Fig. 2.76).

From the diamine, the diisocyanate is formed from the acid-catalyzed reaction with phosgene to form the carbamoyl chloride, which converts to diisocyanates upon heating. As usual, the amine is in equilibrium with the hydrochloride salt formed by the evolved HCl, which requires the use of excess phosgene and heat to liberate the free amine (Fig. 2.77) [157].

IPDI IPDI is prepared by a multistep process beginning with the base-catalyzed aldol condensation of acetone to form isophorone isomers (Fig. 2.78) [158]. Isophorone is subsequently converted to isophorone nitrile by reaction with hydrogen cyanide (Fig. 2.79) [159] and converted to diamine by catalytic reductive amination, followed

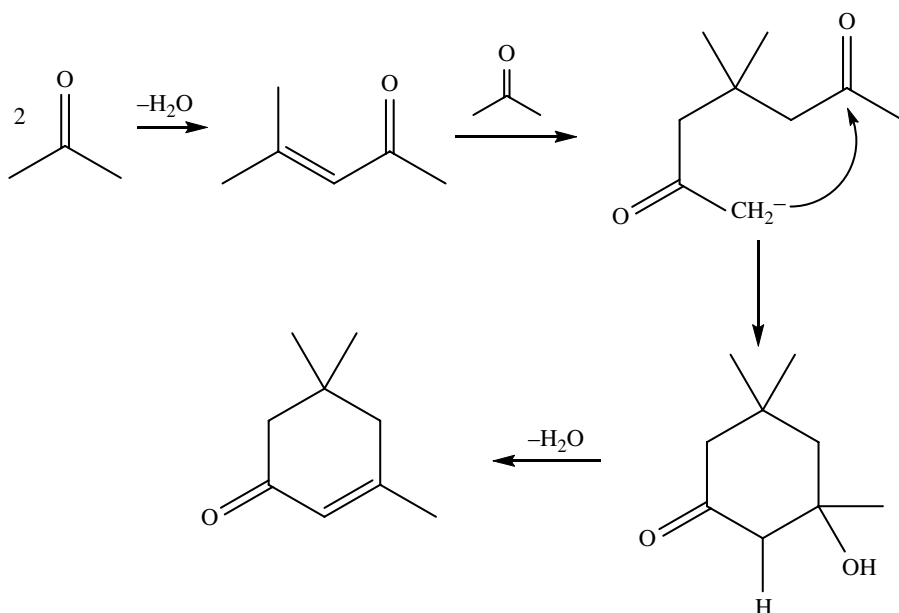


FIGURE 2.78 Trimerization of acetone to form isophorone [161].

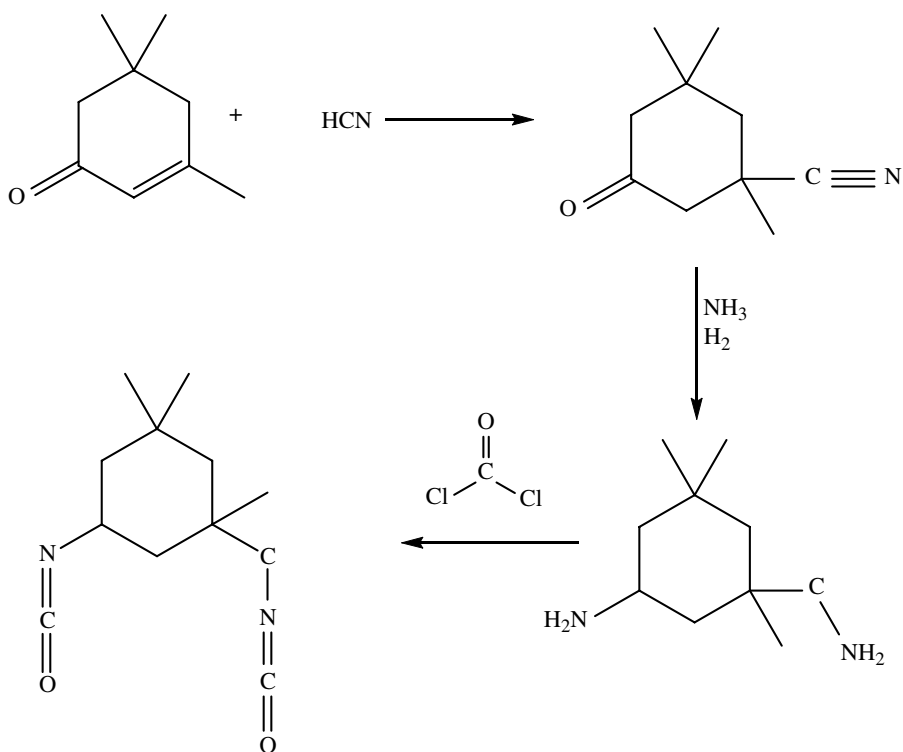


FIGURE 2.79 Conversion of isophorone to isophorone nitrile, hydrogenation to isophorone diamine and subsequent phosgenation to isophoronediiisocyanate.

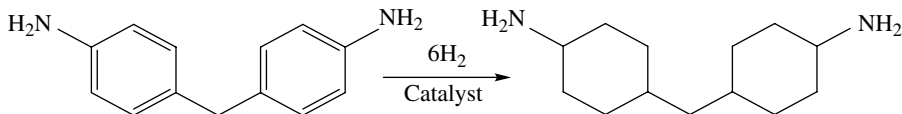


FIGURE 2.80 Conversion of MDA to hydrogenated MDA.

by formation of the isocyanate with phosgene [160]. IPDI is formed in *cis/trans-isomers* of the reactive centers believed to have equal reactivities. The *nonequivalent isocyanate locations* make for differential reactivity with the secondary isocyanate being more reactive due to steric factors. This reactivity difference is a valued attribute of IPDI since it allows for controlled and lower viscosity prepolymers (Section 2.17).

4,4'-Diisocyanatodicyclohexylmethane (H_{12} MDI) Unlike HDI and IPDI, H_{12} MDI derives from the urethane industrial base—the aniline/formaldehyde process to MDA. The economics and price sensitivities therefore mirror those of MDI and its feedstocks. The process to make H_{12} MDI follows that of MDI up until the phosgenation step. At that point, a pure 4,4' MDA cut is distilled from the crude pMDA and hydrogenated [162].

Along with the predicted and desired reaction shown in Figure 2.80, other reactions can occur. One of the most common is deamination resulting in a monoamine. At lower temperatures and pressures, incomplete conversion to aliphatic structures is most common with one ring aliphatic and the other aromatic. This tendency for incomplete hydrogenation is a significant roadblock to expansion of the hydrogenation to the crude pMDI stream as produced. The hydrogenation is done in alcohol or dioxane media using rhodium or ruthenium on alumina catalyst [163, 164]. The use of more common hydrogenation catalysts will often entail the requirement of higher temperatures and the concomitant deamination.

2.2.3.2 Use of Aliphatic Isocyanates The primary uses of aliphatic isocyanates are in coating applications (see Chapter 10) because of their preferred weathering performance relative to aromatic building blocks [165–167]. However, along with weathering, coatings often must also provide other properties such as optical clarity, a high glass transition temperature, and barrier to a variety of chemicals the coating may encounter in use. The ability of isocyanates to form cross-linking structures by self-reaction is made use of in this instance [168, 169]. The mechanism of these cross-linking reactions is covered in detail in Chapter 3. The most common cross-linking applied to aliphatic isocyanates and particularly for coating applications is their processing to isocyanurates (Fig. 2.81) [170–172].

Unlike dimer formation, the trimer is a nonthermoreversible structure. Trimer formation is highly exothermic with a heat of reaction estimated to be 42 kcal/mol of trimer. Since trimerization of difunctional isocyanates leaves free isocyanates to participate in further trimerization, the conditions of reaction have to be controlled to limit oligomerization. Along with providing increased cross-link density, it enhances flame retardancy [173], thermal resistance [174], and chemical resistance [175]; enhances film forming [176]; and improves worker safety [177] by reducing isocyanate vapor pressure. By virtue of the cross-link density, polyurethane-phase separation processes are inhibited, and desirable amorphous coatings are promoted.

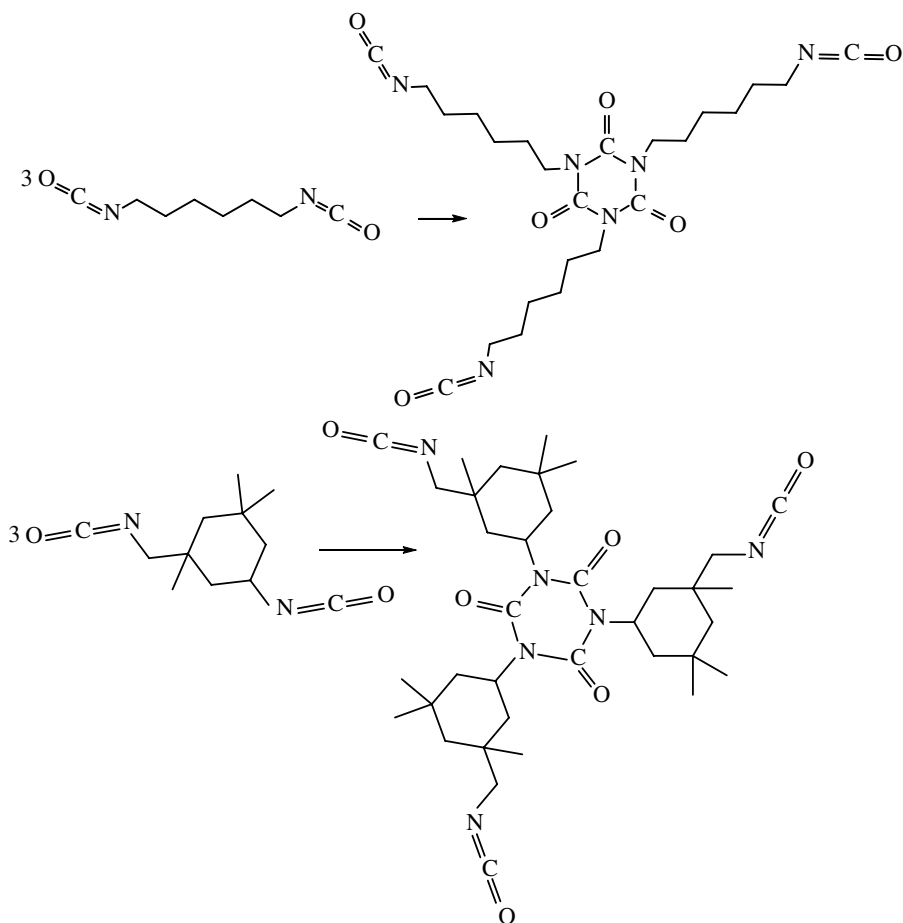


FIGURE 2.81 Trimerization of aliphatic isocyanates for commonly preceding their use in coatings formulations.

Distinguishing the aliphatic isocyanate monomers based on structure is difficult because HDI is seldom used as a monomer but is usually used in the trimer form, so its application is substantially as a cyclic. IPDI is used both as a monomer and in its trimer form, and H_{12}MDI is used almost exclusively in its monomer form. As such, there is a significant overlap in the resulting polyurethane properties, and customers will often use one or the other based on preference. It is also quite common to mix aliphatic isocyanates for formulation optimization [178]. Forming of mixed trimers has also been reported. In this case, the mixture randomization is achieved by staged addition of isocyanates to compensate for the differences in isocyanate reactivity (for instance, IPDI is somewhat more reactive than HDI).

Although the great majority of aliphatic isocyanates are produced via phosgene chemistry, the higher prices commanded by aliphatic isocyanates has allowed non-phosgene routes to diisocyanates to realize industrial reality. Conversion of IPDA to

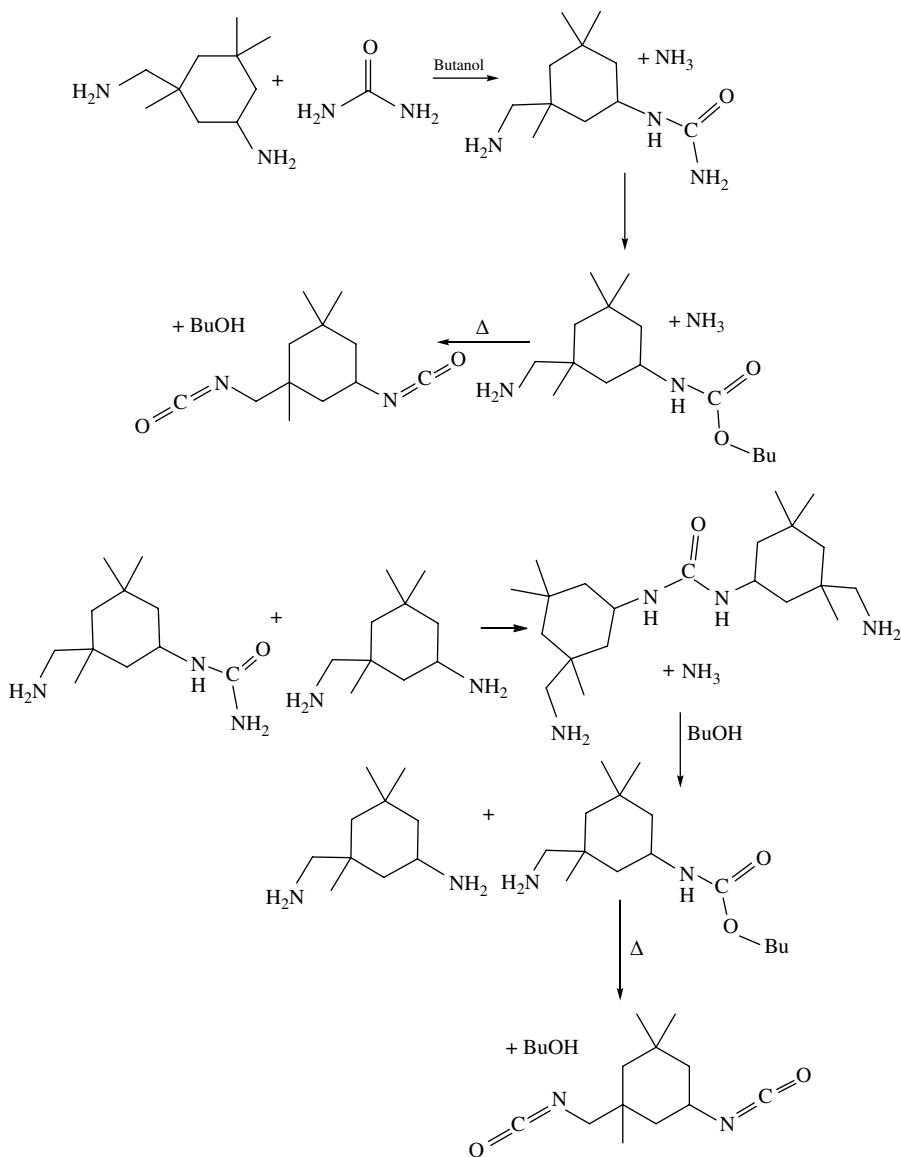


FIGURE 2.82 Conversion of isophorone diamine to isophorone diisocyanates using urea and aliphatic alcohol reagents to form products. Reaction pathways are speculative.

IPDI via reaction with DMC to form the biscarbamate followed by thermolysis to the isocyanate and methanol (see Section “Thermolysis of Carbamic Acid, *N,N'*-(4-Methyl-1,3-Phenylene)Bis-, *C,C'*-Dimethyl Ester Made from the Reaction of Toluene Diamine with Methyl Carbonate”) has been practiced commercially by Daicel Chemical (Japan). Degussa has produced IPDI by reaction of IPDA with urea

and alcohol to form the diisocyanates and ammonia by-product (Fig. 2.82). The mechanism of this route is potentially complex with many possible routes to go from products to reactants. Problems associated with this route have been relatively slow rates at low temperatures and the formation of polyureas at high temperatures. A series of patents document procedures for efficiently producing high yields of the desired diisocyanates [179–181]. A series of reaction pathways or reactants to products is offered in Figure 2.82 [182].

An additional route involves the formation of a carbamate by reaction of urea with an alcohol (see Chapter 12) and substitution of the target amine for the unsubstituted carbamate.

2.3 CHAIN EXTENDERS

For any given polyurethane, soft segments and isocyanates may make up more than 95% of the polymer volume. Very often, a low-molecular-weight component is added that primarily serves as a spacer between neighboring polyisocyanates. Thus, the polymer structure will be, for instance, soft segments of 1000 or 2000

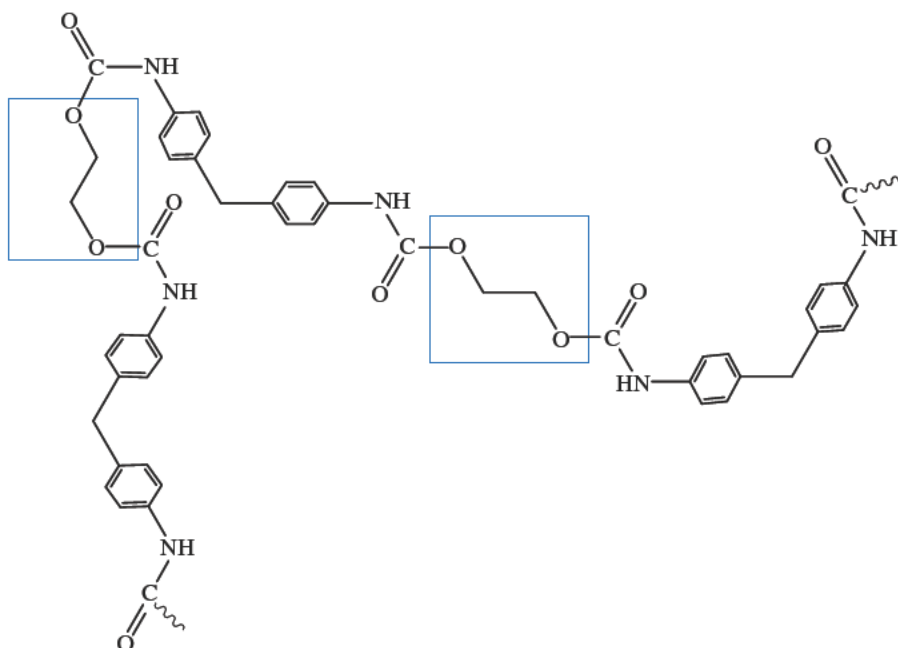


FIGURE 2.83 Ethylene glycol chain extender (in boxes) linking isocyanates through urethane bonds.

molecular weight and hard segment consisting of diisocyanates of 250 g/mol (as in the case of 4,4' MDI) strung together with a short-chain diol or diamine of about 100 g/mol. The low-molecular-weight diol or diamine stringing together diisocyanates is called the “chain extender.” Figure 2.83 is a representation of this concept with an ethylene glycol chain extender. These chains of polyisocyanate and chain extender (ethylene glycol here) are termed the “hard segment.” The end isocyanate units of the hard segments are implicitly connected to high-molecular-weight polyether or polyester soft segment polyols. The importance of this structural detail is that as the addition polymerization occurs, these hard segments, and their immiscibility with the soft segment, drive the phase structure of the resulting polyurethane (see Chapter 4) [183]. The chain extender then has a significant effect on the kinetics and extent of phase separation in these systems. The chain extender can also have a significant effect on the strength of the hard segment phase (similar to a crystal-phase melting point) by virtue of the interphase hard segment hydrogen bonding (see Fig. 2.84) [184].

Thus, the chain extender structure can have a significant effect on polyurethane properties by its ability to drive phase separation, its ability to complement or interfere with a regular hard segment structure, and its ability to promote interhard segment hydrogen bonding [185–189]. Virtually any low-molecular-weight polyfunctional molecule capable of reacting with isocyanates has been explored for its influence on polyurethane properties. The most prevalent and industrially important chain extender in foams is water, which makes urea hard segment and 1,4-butanediol used commonly for elastomer hard segments. The urea units can be particularly robust due to the presence of the bidentate hydrogen bonding available to the interchain structure as seen in Figure 2.85. While the most common source of urea hard segment is obtained by the reaction of isocyanate and water, an alternative source is from the reaction of isocyanates and amines. Hydroxyl functional chain extenders can also serve as cross-linkers. In contrast, secondary amines offer a single isocyanate reaction site and the possibility of maintaining melt processability.

There are a huge number of potential chain extenders that can be employed to alter hard segment structure, polymerization kinetics, and polymer properties. Table 2.13 is a limited list sampling the numerous types and structural parameters of each. The potential effects on properties is covered in Chapter 4 and chapters associated with polymer properties.

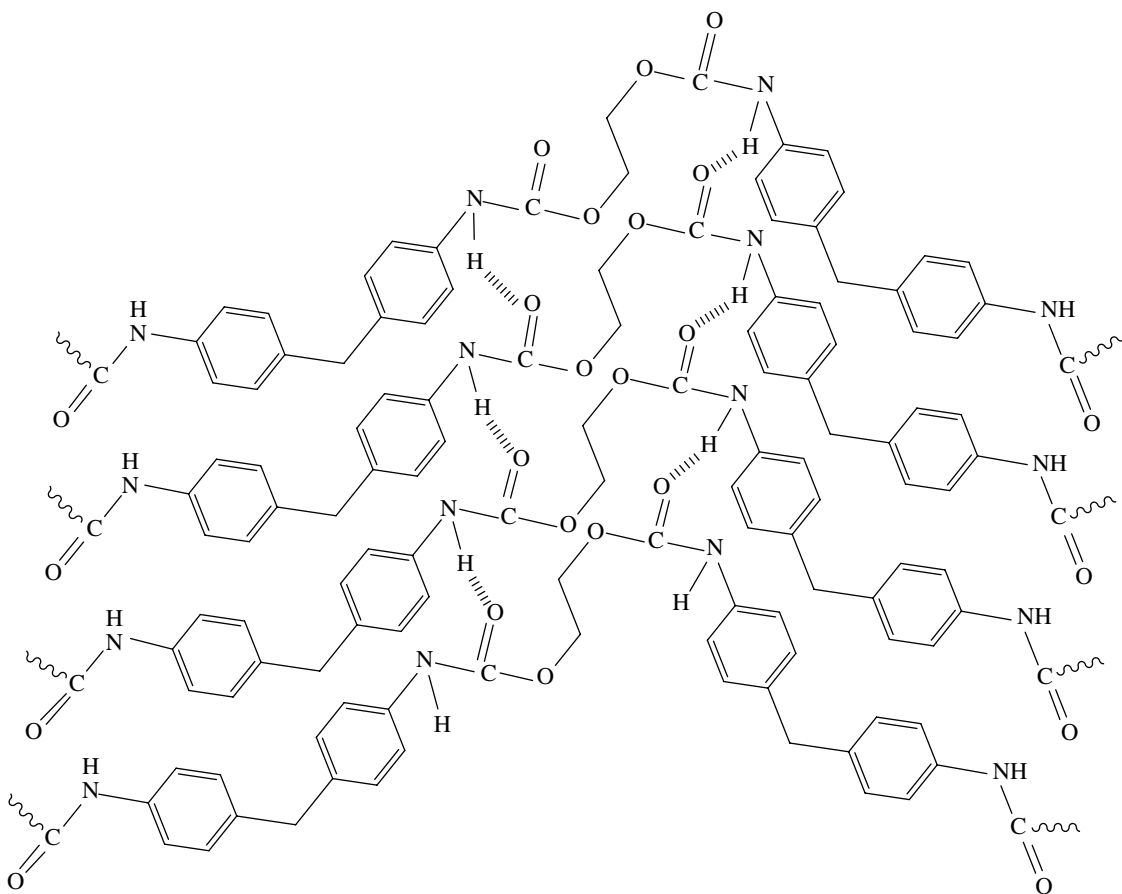


FIGURE 2.84 Hydrogen bonding between chain extended urethane hard segments. Cohesive energy between hard segment chains is influenced by the chain extender, by the spacing between H-bonding interactions, and the regularity of the assembled chains into quasi-crystalline structures. Irregularities in hard segment structure can lead to a more nematic-like liquid-crystal structure.

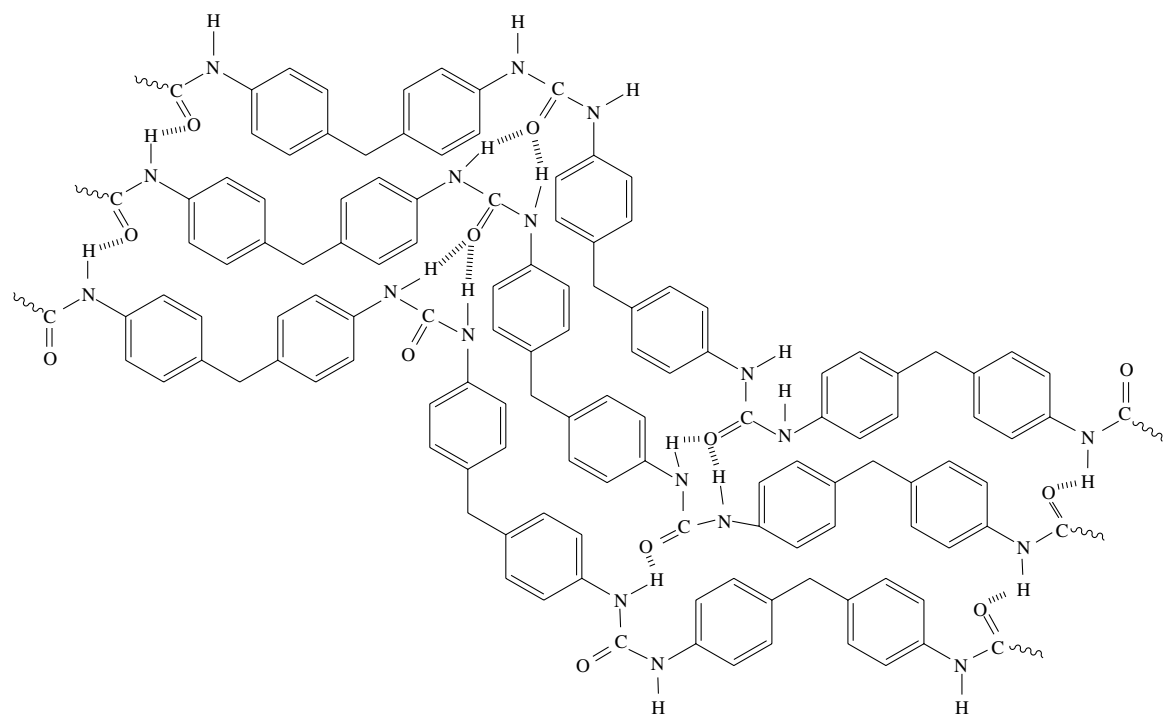
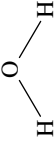
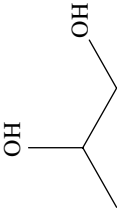
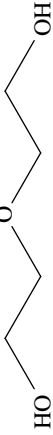
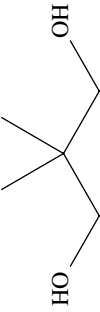
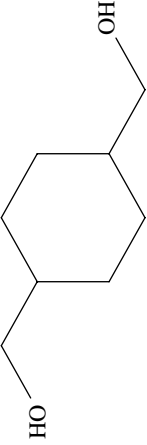


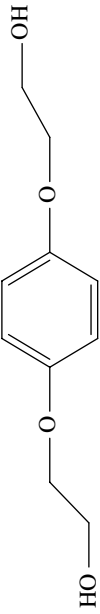
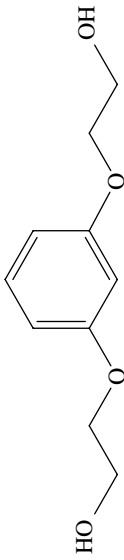
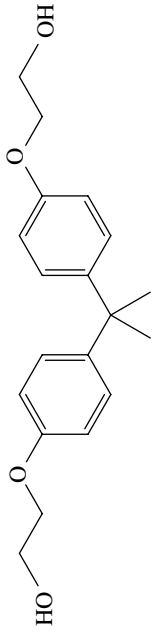
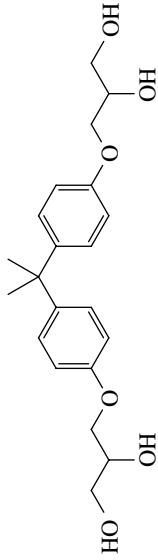
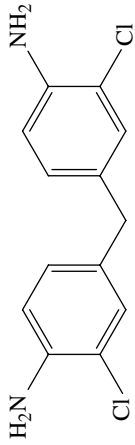
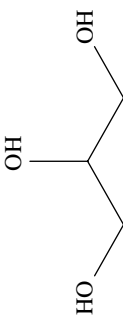
FIGURE 2.85 Illustration of the origin of the greater stabilization of hard segments afforded by urea chain extension versus the urethane chain extension shown in Figure 2.83.

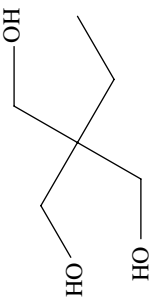
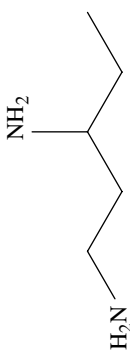
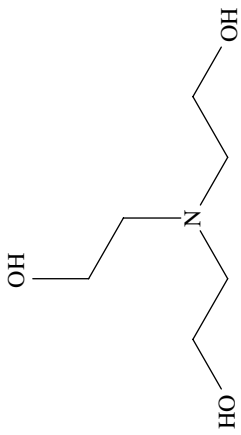
TABLE 2.13 Structure and properties of common chain extenders used in urethane chemistry

Chain extender/cross-linker	Structure	Mol wt g/mol	Equiv. wt g/eq	OH/NH number
Water		18	9	6233
Ethylene glycol		62	31	1808
1,2-Propylene glycol		76	38	1475
1,3-Propylene glycol		76	38	1475
Diethylene glycol		106	54	1057
Neopentyl glycol		104	52	1078
Butanediol		90	45	1244
Hexanediol		118	59	951
Cyclohexane dimethanol		144	72	779

(Continued)

TABLE 2.13 (Continued)

Chain extender/cross-linker	Structure	Mol wt g/mol	Equiv. wt g/eq	OH/NH number
Hydroquinone bis(2-hydroxy ethyl)ether		198	99	567
Resorcinol bis(2-hydroxyethyl)ether		198	99	567
Bisphenol A bis(2-hydroxyethyl)ether		316	158	355
Bisphenol A bis(2,3-dihydroxypropyl)ether		376	94	597
4,4'-Methylenebis(2-chloroaniline) (MOCA)		267	133.5	420
Glycerine		92	31	1828

Trimethylolpropane		134	45	1247
1,6-Hexane diamine		116	58	967
1,3-Diamino pentane		102	51	1100
Diethanolamine		105	35	1602
Triethanolamine		149	50	1122

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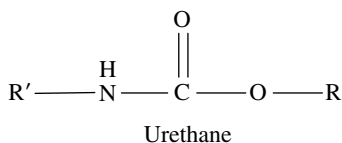
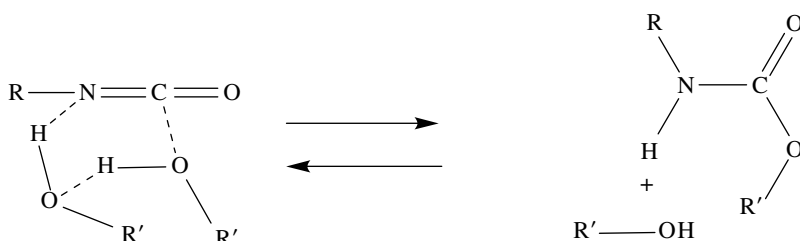
3

INTRODUCTION TO POLYURETHANE CHEMISTRY

3.1 INTRODUCTION

In principle, this chapter should be a simple matter of discussing the means of achieving the urethane structure (Fig. 3.1); however, given the reactivity of polyurethane chemical building blocks and the kinetics of the urethane forming reaction, many other structures form, and these can have significant effects on the final materials. In some cases, the experimental approach is to control variables to a level that optimizes the final product and its structure. In other cases, the reaction is allowed to follow its course, find equilibrium, with the object to simply achieve a desired level of reproducibility. This chapter will cover the mechanism and catalysis to polyurethane structure, the side reactions that can take place, and the results these variances can have on the final product. Also covered are the means of minimizing some routes, maximizing others, and the properties achieved in such control. Only isocyanate-based reactions will be covered in this chapter while other routes to urethane will be covered in Chapter 12.

Although isocyanates are reactive species, at room temperature isocyanate reacts with hydroxyl relatively slowly. To some extent, the slow speed is a reflection of phase incompatibility of the relatively nonpolar and denser isocyanate phase, and the relatively polar and less-dense polyol phase (hydroxyl components). However, even when phase compatibilized with a surfactant, the reaction is slow at room temperature. In general, when simply allowed to sit in each other's presence, a hydroxyl unit and an isocyanate will slowly form urethane or urea (in the case of

**FIGURE 3.1** Urethane structure.**FIGURE 3.2** Generally accepted transition state for uncatalyzed formation of urethane.

reaction with water) at the interface, forming a crystalline barrier, which slows the observed reaction rate further. For this reason, it is commonplace and industrially essential to utilize catalysts and provide some method of phase mixing to enhance the reaction rate between hydroxyls and isocyanates. Even in the presence of catalysts, isocyanate reactions can show sharp temperature threshold behavior. Observations such as these have created numerous theories about the action of catalysts in these systems. In the absence of catalyst, it is believed that urethane formation proceeds through a six-member ring transition state [1, 2] (Fig. 3.2). The simplest transition state would be a four-member ring, unmediated by an additional third body (i.e., second alcohol) [3, 4]. Several points argue against this. The first is that Fourier transform infrared spectroscopy (FTIR) analysis shows that polyols are predominantly in a hydrogen bonded state suggesting that the availability of lone OH groups may be a limiting factor. Figure 3.3 shows FTIR spectra for a 1000 equivalent weight commercial polyol. The spectra focus on the relevant OH stretch region. The breadth of the peak centered at 3500 cm^{-1} is indicative of the extensive hydrogen bonding these molecules engage in. An OH group that was uninvolved in intermolecular interactions would reveal itself at about 3650 cm^{-1} [5] and would increase its intensity as a function of temperature. The absence or very slight population indicated by the peak intensity and the temperature independence of the response ($25\text{--}85^\circ\text{C}$) indicate very little free OH under these conditions. Additionally, quantum mechanical calculations predict that the expected rate of reaction in the absence of bond polarization (as shown in Fig. 3.2) is a much slower reaction than observed. However, when mediating influences such as shown in Figure 3.2 are introduced, the observed and calculated reaction rates are in good agreement [6].

Along with self associations, there are a large number of structural and experimental factors that can influence the rate of reaction. One of the main factors is isocyanate structure since it was first shown that phenyl isocyanate is nearly a factor

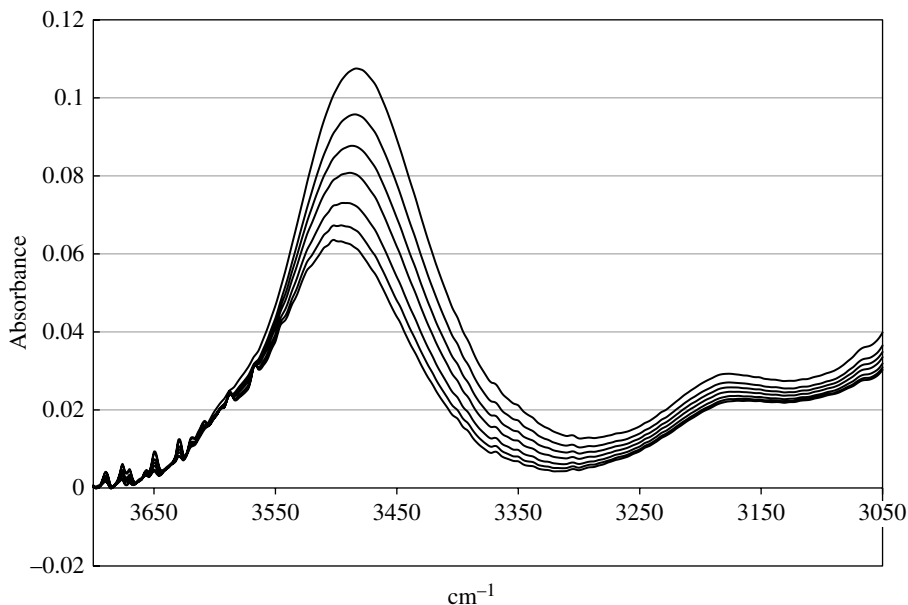


FIGURE 3.3 Fourier transform infrared spectroscopy of a polyether polyol focusing on the OH stretch region. The nested spectra are the evolution of the signal from 25 (top curve) to 85°C (bottom curve) in 10°C increments.

of 50 more reactive with an alcohol than ethyl isocyanate with the same alcohol [7–9]. This has inevitable consequences for the application of aliphatic isocyanates in weatherable formulations. In addition, it has been proposed that the reaction rate might depend on the dielectric strength of a solvent environment. The rate of reaction can decrease with increasing solvent dielectric strength [10–12] and also can be strongly affected by the solvent's ability to associate with hydroxyls through polar or hydrogen bonding interactions[13, 14], thereby decreasing the availability of hydroxyl functionality to react with the isocyanate.

3.2 MECHANISM AND CATALYSIS OF URETHANE FORMATION

There are a large number of molecules and unique structures that catalyze urethane reactions. Examples are shown in Figure 3.4 along with their commercial names. Many others are available as well [15]. The mechanism of their action is a subject of debate. The structures of Figure 3.4 can be conveniently broken into Lewis acid transition metals and tertiary amines. Mechanisms of action of the two classes of catalyst are postulated to proceed by different routes. Basic models usually have the catalyst polarizing either the hydroxyl or the isocyanate moieties via simple polar interactions (Fig. 3.5). One can expect that catalyst removal of electron density from the oxygen or nitrogen of the NCO group will in turn enhance the

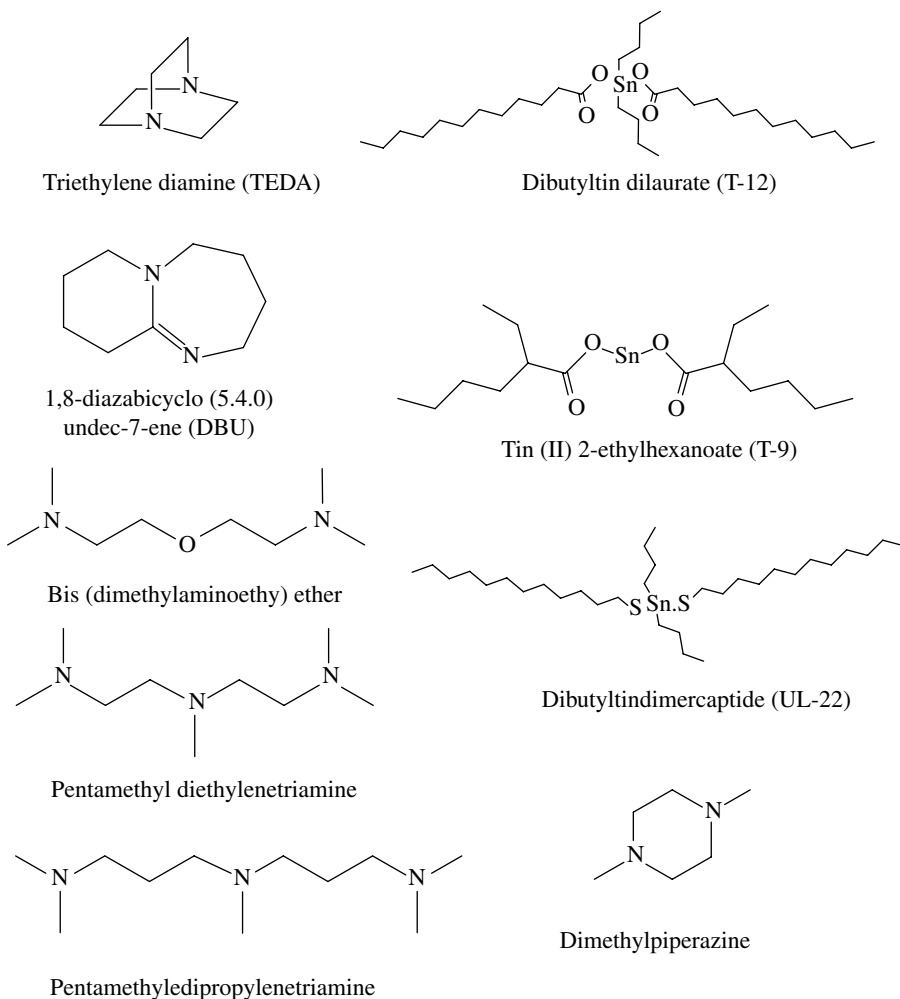


FIGURE 3.4 Common catalysts for urethane and urea formation. Trade names are in parentheses.

electrophilic (electron deficient) character of the isocyanate carbon. This effect will not only increase the rate of urethane formation consistent with the structure of Figure 3.2, but may also influence the myriad side reactions isocyanates undergo, a topic that will be covered at greater length later in this chapter. Alternative mechanisms of catalyst action have also been proposed [15–20]. In many of these studies, the mechanism of action was probed by controlling catalyst concentration or catalyst activity (i.e., by varying acidity for instance). These mechanisms can sometimes be quite elaborate and still be compelling based on presented evidence. A mechanism of Lewis acid metal catalyst activity has been presented by several independent workers (Fig. 3.6) [16, 17]. This mechanism has a unique attribute in

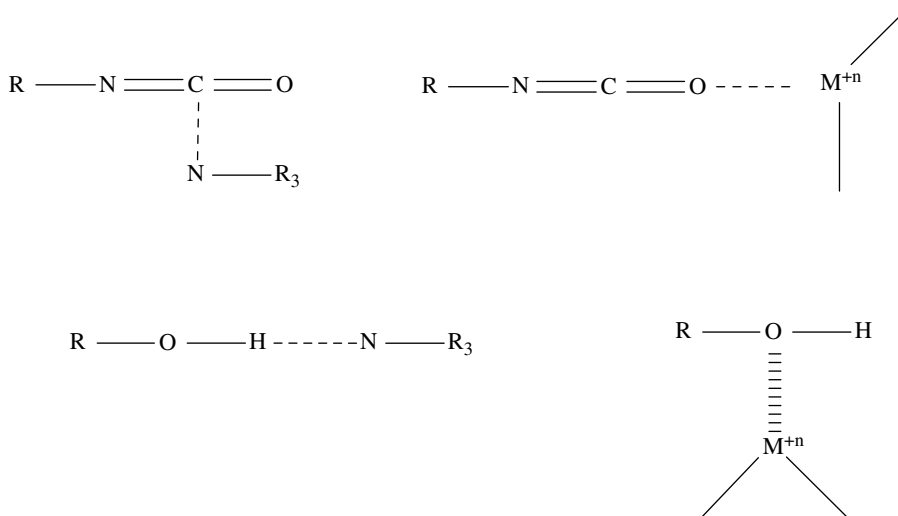


FIGURE 3.5 Examples of bond polarization mechanisms of catalytic action.

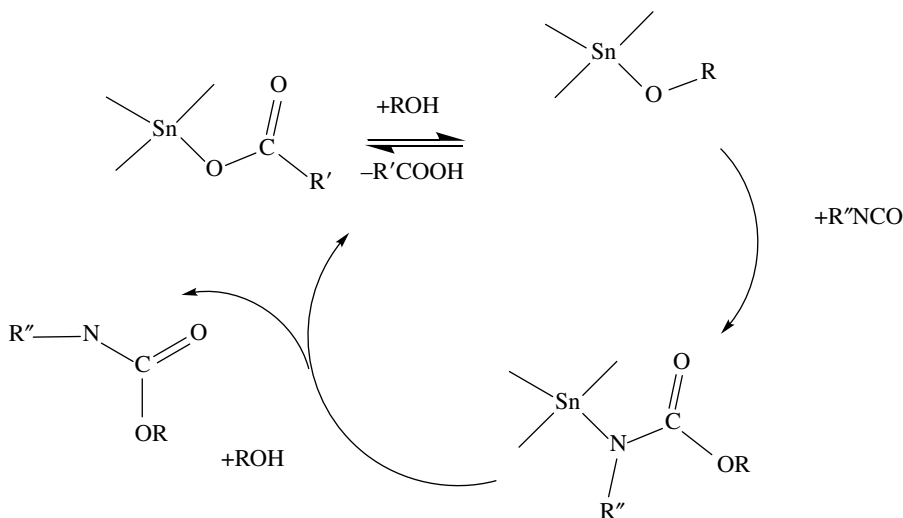


FIGURE 3.6 Proposed mechanism of Lewis acid catalysis of urethane formation.

that its initial assumption is based on the metal's ability to increase its complexation number and increase reactivity of the associated ligands. It also presents opportunities to probe its validity by varying structures and concentrations of the reactants to see if the expected influence is realized. This deductive approach has had mixed mechanistic success since the kinetics have been observed independent of the ligand acid strength and is as well independent of the presence of total system carboxyl or carboxylate strength. Thus the validity of the mechanism rests

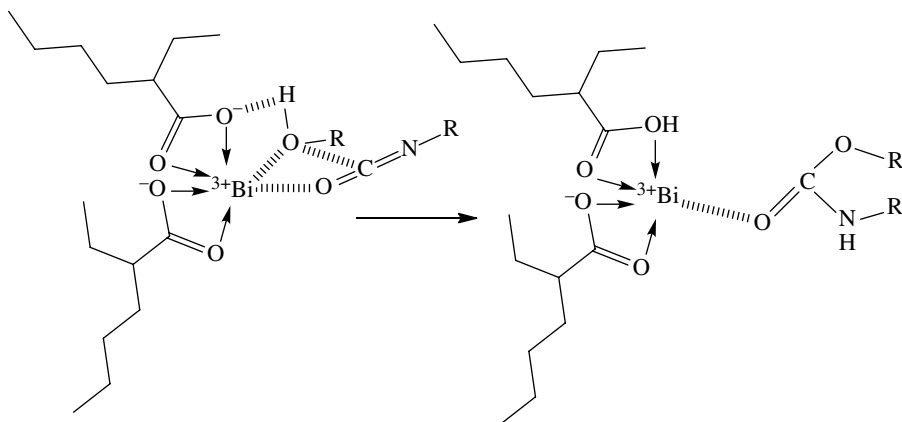


FIGURE 3.7 Proposed mechanism of bismuth carboxylate urethane catalysis. Coordination of the metal is simplified for illustrative purposes.

on the formation of the alkoxide form of the catalyst. The thermodynamics of this transformation has been evaluated, and NMR data based on significant downfield OH proton shifts and line broadening in the presence of bismuth carboxylate catalysts suggest that the alcohol is both coordinated and undergoing proton exchange in the presence of catalyst. Such data suggest the mechanism illustrate in Figure 3.7 to explain this result [18].

Due to difficulties associated with (i) making highly controlled measurements, (ii) the catalytic (albeit weak) action of the product urethane groups formed, (iii) the difficulty quantifying the effects of varying associations of reactants and products affecting the rate constants, and (iv) the overall thermal sensitivity of the reactions and the catalysis, it is likely that a defined Lewis acid catalyst mechanism enjoying universal endorsement will remain elusive.

The mechanism of tertiary amine catalyst action is also unsettled and further complicated by the tendency of amines to drive reactions other than urethane formation [21–24]. In fact almost all amines are capable of promoting the formation of urethane, urea (reaction of water or amine with two isocyanates), and numerous crosslinking side reactions of isocyanates with reaction products. The catalytic activity forming urethane bonds is conventionally referred to as the “gel” reaction since in polyurethane chemistry the urethane reaction is most tied to the rapid growth of molecular weight and concomitant increase in viscoelasticity resulting in gelation. The catalyzed reaction of isocyanates with water is referred to as the “blow” reaction due to the formation of carbon dioxide which contributes to the formation of foam or frothed morphologies [25]. As shown in Figure 3.5, the ability of tertiary amines to interact strongly with both hydroxyl and isocyanate groups accounts for their versatility in polyurethane chemistry. Amines can also be designed to preferentially interact with water accounting for the ability of some amines to drive the blow reaction with much higher efficiency than the gel reaction (Fig. 3.8).

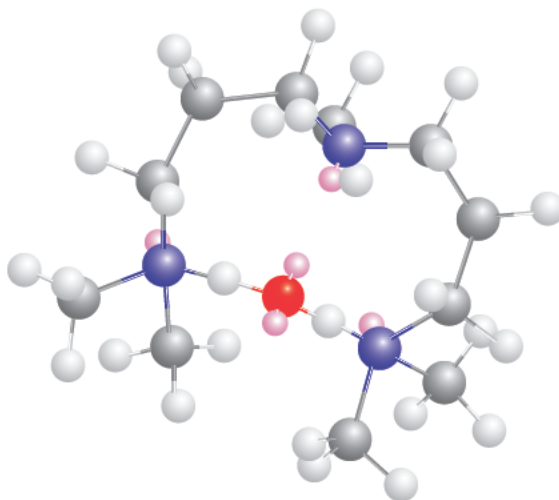


FIGURE 3.8 Energy minimized interaction between water and pentamethylene dipropyl-enetriamine demonstrating the favorable water interactions that result in good blow catalyst properties (light red surfaces indicate non-bonding electron pairs, red is oxygen, and blue is nitrogen). (See insert for color representation of the figure.)

It is also easy to visualize how a polyamine catalyst can interact simultaneously with a water (or polyol hydroxyl) and an isocyanate to rapidly promote their reaction with one another; however, it is difficult to predict *a priori* what the behavior of a given amine will be based on measurables like basicity or even steric hindrance [24, 26, 27]. Once an amine is measured for overall activity and blow/gel reaction ratio, the connection is usually then asserted.

At the same time that amine catalysts are able to promote both blow and gel reactions, they are also capable of promoting numerous side reactions. Most of these side reactions involve the reaction of isocyanates with already formed reaction products, and their efficiency for any given side reaction will depend on isocyanate concentration, co-reactant concentration, temperature, catalyst concentration, etc. Isocyanate side reactions will be covered in greater detail later in this chapter. One isocyanate reaction that has great industrial relevance, and uses entirely different catalysts than amines or heavy metals, is the trimerization of isocyanates to isocyanurates (Fig. 3.9). Isocyanurates are particularly useful in the manufacture of construction foams because of their contribution to network crosslink formation, their thermal resistance, and their relative inflammability.

While some amines can catalyze isocyanate trimerization, the temperature at which they are efficient can be high enough that many other reactions are also operating. In general, excellent trimerization catalysts are highly basic and nucleophilic [28–30]. One hypothesis is that they operate through a stepwise addition beginning with nucleophilic attack of the catalyst on the carbon of a first isocyanate. This increases the nucleophilicity of the neighboring nitrogen to then react with a carbon on a second isocyanate and culminates with the rapid ring closure to the six-member isocyanurate ring.

3.3 REACTIONS OF ISOCYANATES WITH ACTIVE HYDROGEN COMPOUNDS

Polyurethanes are the product of mixing isocyanates with hydroxyls and the structure is shown in Figure 3.1. This is a relatively straightforward addition reaction; however, side reactions can occur having profound effects on polyurethane properties. There is no condensation elimination product in the formation of polyurethane, and the product is in a strongly temperature-dependent equilibrium with reactants (isocyanates and hydroxyl compounds [33, 34]. Literature references report a heat of formation ranging from -16 to -34 kcal/mol. Most of the data ranges from -22 to -25 kcal/mol [35] and is only slightly dependent on the alcohol (primary or secondary) and structural aspects of the isocyanate (Table 3.1) [36, 37]. However, as shown in Figure 3.3, reactants may exist in varying states of self association and the heat of disassociation, and hydrogen bonding will vary in measurement and calculations as well.

TABLE 3.1 Enthalpy of urethane formation (kcal/mol) of various isocyanates with varying alcohol order

	<i>n</i> -butyl	Isobutyl	Sec-butyl
Phenyl isocyanate	25.1	24.1	23.4
<i>o</i> -tolyl isocyanate	23.5	22.1	21.7
<i>m</i> -tolyl isocyanate	19.5	19.1	18.5
<i>p</i> -tolyl isocyanate	24.7	23.9	23.6
2,4 toluene diisocyanate	22	21.3	20.6

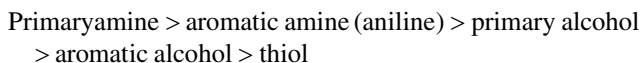
TABLE 3.2 Approximate reversion temperatures of urethane product back to constituent isocyanates and polyols^a

Urethane structure	Approximate limit of thermal stability (°C)
$\begin{array}{c} \text{H} \quad \text{O} \\ \quad \\ \text{Alkyl} - \text{N} - \text{C} - \text{O} - \text{Alkyl} \end{array}$	250
$\begin{array}{c} \text{H} \quad \text{O} \\ \quad \\ \text{Aryl} - \text{N} - \text{C} - \text{O} - \text{Alkyl} \end{array}$	200
$\begin{array}{c} \text{H} \quad \text{O} \\ \quad \\ \text{Alkyl} - \text{N} - \text{C} - \text{O} - \text{Aryl} \end{array}$	180
$\begin{array}{c} \text{H} \quad \text{O} \\ \quad \\ \text{Aryl} - \text{N} - \text{C} - \text{O} - \text{Aryl} \end{array}$	120

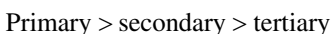
^aFrom Ref. [41].

The urethane bond is able to undergo reversion back to isocyanate and hydroxyl functionality at elevated temperatures [38–40]. The temperature at which this reversion commences is a function of the stability of the urethane structure from which reversion is occurring. Table 3.2 provides the detail of the structural aspects contributing to urethane thermal stability. The greater the aliphatic content of the structure, the more thermally stable, since aromatic delocalization can stabilize the activated states from which reversion results [9]. It has been observed that diphenylmethane diisocyanate (MDI)-based urethanes have higher thermal stability relative to toluene diisocyanate (TDI). Urethanes from aromatic alcohols exhibit particularly low thermal stability and for this reason phenol has been widely used as a blocking agent for protecting isocyanate groups and making them available at elevated temperatures ($>100^{\circ}\text{C}$) [42, 43]. In the absence of a change in stoichiometry (for example due to selective volatilization or degradation of one of the reactants), upon cooling the formation of urethane is highly favored and there is little or no change in the overall molecular weight [44]. Figure 3.11 shows a temperature-dependent dynamic mechanical analysis demonstrating the loss of modulus and the increasingly liquid-like behavior as reversion reactions become increasingly prevalent at temperatures above 120°C .

It is generally accepted that the reactivity of an active hydrogen compound will increase as its nucleophilicity increases (and so reactivity with the isocyanate carbon increases). The general trend follows the sequence [10]:



The low reactivity of thiols with isocyanates perhaps reflects the low dipole moment of the S–H bond instead of the nucleophilicity. Within each grouping, important steric influences can occur. For instance, the measured reactivity of alcohols follows the sequence:



The ratio is 200:60:1 [45] and has been determined by the measurement of the reaction rates of isocyanate with butanol variants.

The effect of isocyanate structure on reactivity can be understood in terms of the relationship of electronic and steric factors affecting the NCO groups. Quantum mechanical calculation on hydrogen isocyanate (isocyanic acid) $\text{H}-\text{N}=\text{C}=\text{O}$ resulted in relative charge values of $\text{H}:+0.29$ $\text{N}:-0.17$ $\text{C}:0.51$ $\text{O}:-0.34$ [46]. In general, electronic factors that decrease the electron density on the carbon will increase the isocyanate reactivity. In addition, from the relative charge values, it is reasonable to conclude that increasing the negative charge density on the isocyanate oxygen will increase reactivity by electrophilic attack. While that will be true, it has also been calculated that the isocyanate nitrogen is actually the favored position for attack due to the greater spatial dispersion of electronic charge around the oxygen. If steric factors are held constant, any electron-withdrawing group attached to the nitrogen enhances the electrophilic character of the isocyanate carbon resulting in the relative reactivity ratios

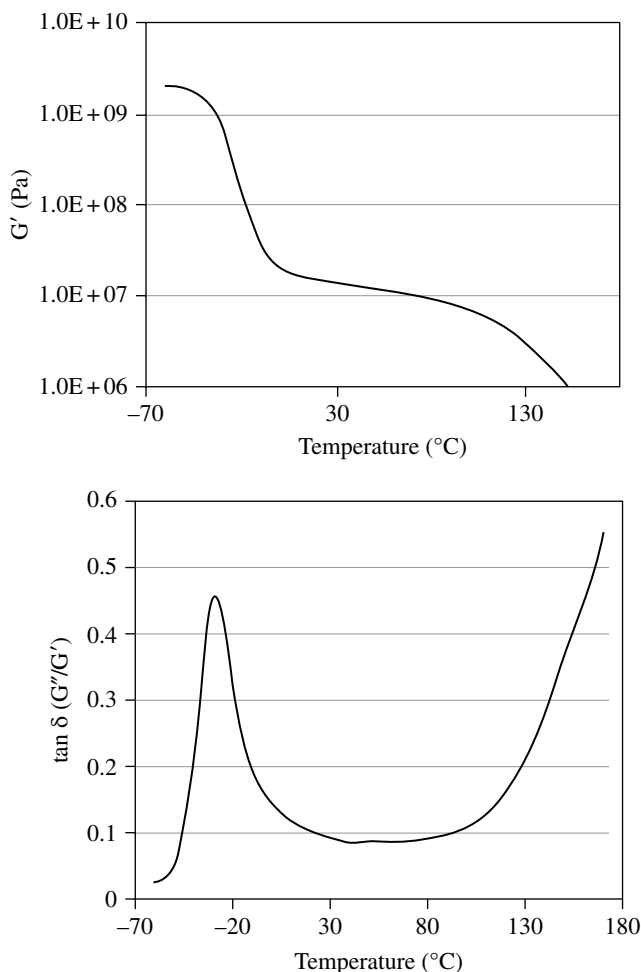


FIGURE 3.11 Dynamic mechanical analysis of an aromatic polyurethane showing the loss of modulus and increase in viscous (liquid-like) behavior at temperature above 120°C reflecting the reversion reaction.

shown in Table 3.3. Toluene diisocyanates are not shown in Table 3.3 due to the significant reactivity difference of the second isocyanate upon reaction of the first isocyanate, and the significant difference in the reactivity of the isocyanate group depending on the ring position [47]. This is further complicated by the practical fact that most commercially available toluene diisocyanates are mixtures of 2,4- and 2,6-diisocyanate isomers. The relative reactivity of these isomers and of the second ring isocyanate following the reaction of the first is given in Table 3.4. This deactivation results from the replacement of a strongly activating isocyanate group (electron withdrawing increasing the reactivity of the isocyanate carbon) with a weakly activating urethane group. The effect of the first isocyanate reaction on the second

TABLE 3.3 Reactivity of several common diisocyanates relative to MDI

Diisocyanate	Reactivity
Para-phenylene diisocyanate	1.85
MDI	1
Isophorone diisocyanate	0.15
1,6 hexamethylene diisocyanate	0.13

TABLE 3.4 Reactivity of the isocyanates of toluene diisocyanate isomers relative to the para position (fourth position) of the 2,4 isomer

Isocyanate	k_1	k_2
2,4 TDI	100	12
2,6 TDI	56	17

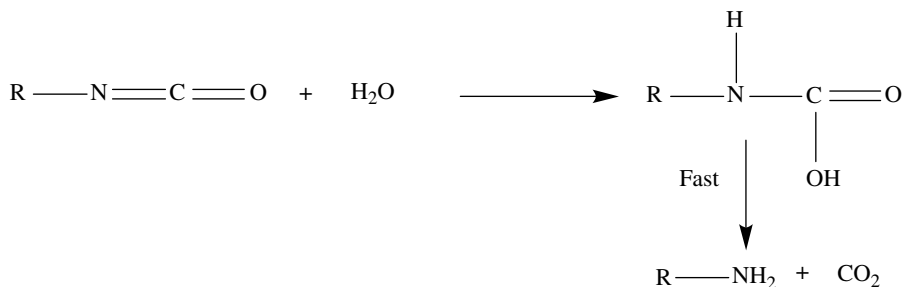
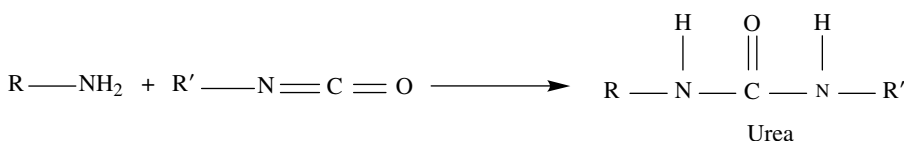
for 4,4' MDI is not as important since they are on different aromatic rings separated by a non-conjugated methylene linkage, but it has been reported that the second reaction may be slowed down as much as a factor of two, though the cause of this retardation is not known.

As alluded to earlier, the effect of solvent on urethane reactions has been noted in the literature [45, 48, 49]. Particular notice was taken when a 71-fold increase in rate was observed in acetonitrile versus benzene [45]. While it was initially thought that this was a result of the solvent dielectric strength, it was subsequently shown that the activation energy for urethane formation was the same in toluene, dibutyl ether, and acetonitrile. Theoretical calculations have also suggested that dielectric strength plays a minor role in urethane formation [2]. It is now thought that the major effect of solvent on urethane formation is the effect of solvent on the hydroxyl phase self-association, and the concentration of free or dimeric alcohol available for reaction. Additional studies have been done to study the effect of catalyst and activation parameters in different solvents at varying conversion [50].

3.3.1 Urea Formation

The reaction of isocyanates and water to form urea is essential to many polyurethane industrial applications. The reaction with water creates the essential stability and heat of reaction to make the kinetics of foam formation practical [51]. In addition, it creates a gas reaction product (CO_2) which provides an expanding volume helping create the porous structure of foams (Fig. 3.12). The initial reaction of water and isocyanate forms an unstable carbamic acid intermediate that immediately decomposes to amine and CO_2 [52].

The reaction of amine with isocyanate is diffusion controlled forming urea and a significant enthalpy of reaction (Fig. 3.13) (ca. 40 kcal/mol) [53]. It is reported that the

**FIGURE 3.12** The reaction of isocyanate and water forming an amine.**FIGURE 3.13** The reaction of amine with an isocyanate to form urea.

use of catalyst has no kinetic effect on the rate of amine and isocyanate reaction and that the reaction of each NCO with water liberates a similar amount of heat as in the urethane reaction. Disparities in the literature may depend on experimental factors affecting the self associations that promote or hinder the formation of the new urea bond.

The reactivity of water with isocyanate relative to that of hydroxyls is generally regarded as following a path similar to that of alcohol hydroxyl requiring the concerted interaction of two water molecules across the isocyanate N=C bond. Quantum mechanical calculations have suggested that a third water molecule would actually provide an enhanced geometry for the reaction across the isocyanate [46]. Certainly, the insolubility of most isocyanates with water will have significant effect on the observed rate of reaction and can conceivably account for much disparity of the measured rates found in the literature [54].

The kinetics of urea formation from the water reaction is of course a convolution of the initial kinetics of isocyanate and water which is slow unless catalyzed, followed by the reaction of the subsequent amine with isocyanate to urea which is diffusion controlled [48]. An interesting phenomenon is the apparent first-order kinetic dependence on isocyanate concentration and second-order dependence on the amine. This second-order dependence on amine is realized for both aniline and aliphatic amines. This high order dependence coupled with the relatively low activation energy (~17.5 kJ/mol) account for the very high initial reactivity of these systems [48].

3.3.2 Allophanate Formation

The reactions described earlier are those based on reactants and intended by the chemist. However, due to the reactivity of the isocyanate group, the adiabatic heat buildup in the reacting mass, and local inhomogeneities in reactant concentration, other

reactions can and do occur. The reaction of an isocyanate and a urethane to form an allophanate is one such reaction (Fig. 3.14) [55]. The active H on the urethane nitrogen is quite a bit less active than those available on water or alcohol resulting in relatively unfavorable kinetics of formation (Table 3.5). Allophanate formation can occur under conditions of elevated temperature and the presence of excess isocyanate in the immediate vicinity of the urethane linkage. However, like the urethane bond, at temperatures above 100–150 °C, the allophanate linkage will revert to the urethane and the free isocyanate reflecting the stability of the parent urethane [56]. It is seemingly inevitable that allophanates form in the practice of making urethanes. The industrial approach has in this case made the best of it by formulating reactant concentrations to optimize the number of allophanate linkages that provides crosslinking to obtain the desired final polymer properties [57, 58]. The gradual increase of polyurethane tensile properties upon cooling over a period of days is sometimes considered a result of slow formation of allophanates (among other possibilities including maturation of phase morphology). Due to the thermal reversibility of the allophanate bond, these crosslinks do not have to negatively affect the processability of the polymer [59].

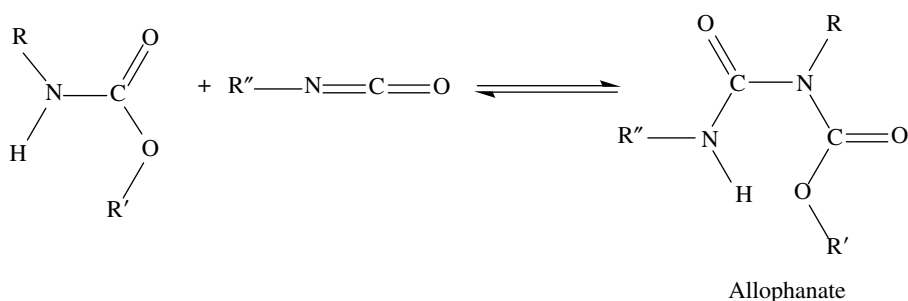


FIGURE 3.14 Formation of an allophanate by reaction of a urethane with an isocyanate. R group can constitute an additional isocyanate moiety resulting in crosslinking.

TABLE 3.5 Relative reaction rates of isocyanates with varying reaction partners

Active H compound	Structure	Relative uncatalyzed reaction rate at 25 °C
Primary aliphatic amine	R-NH ₂	100,000
Primary secondary amine	R ₂ N-H	20,000–50,000
Primary aromatic amine	Ar-NH ₂	200–300
Primary hydroxyl	R-CH ₂ -OH	100
Water	H ₂ O	100
Carboxylic acid	R-COOH	40
Secondary hydroxyl	R ₂ CHOH	30
Urea	R-NH-CO-NH-R	15
Tertiary alcohol	R ₃ COH	0.5
Urethane	R-NH-COOR	0.3
Amide	R-CO-NH ₂	0.1

3.3.3 Formation of Biurets

Just as isocyanate in the presence of urethane at elevated temperatures can create allophanates, isocyanate in the presence of urea can create a biuret linkage (Fig. 3.15). The hydrogen on the urea nitrogen is slightly more reactive than that of the urethane resulting in the biuret linkage having slightly more thermal stability than the allophanate (Table 3.5). Regardless, the biuret linkage is thermo-reversible and has temperature-dependent effects on overall polymer properties [60, 61].

3.3.4 Formation of Uretidione (isocyanate dimer)

The dimerization of isocyanate to form a uretidione is a slow reversible reaction (Fig. 3.16) [62]. Uretidione structures have found industrial use as a crosslinking structure within urethane powder coatings [63, 64], but is otherwise most notable as a problem related to MDI storage. Due to fortuitous packing of MDI in the crystal, the formation of MDI dimers occurs more rapidly in the solid state than in the melt [65]. In fact the rate of formation of MDI dimer is most rapid at normal room temperatures converting approximately 0.01% (wt/day) at 21 °C. For this reason, it is common practice to store MDI either under refrigeration or in the melted state to increase shelf-life and to filter the molten MDI prior to use [66]. Dimer has a nearly zero heat of formation and the disassociation occurs at relatively low temperatures (80–100 °C). This permits uretidione to serve as a protected isocyanate group in a manner similar to that described previously with phenols. This is particularly useful for 2,4 TDI protection since there is a substantial difference in the reactivity of the isocyanates, and the formation of trimer does not present itself as a competitive reaction [10].

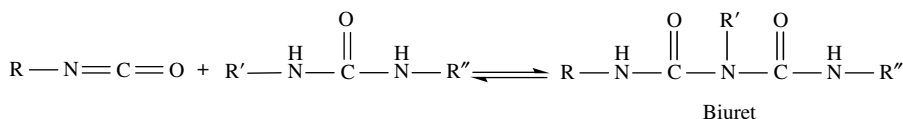


FIGURE 3.15 Formation of a biuret linkage by reaction of urea with isocyanate. The R group can constitute an additional isocyanate moiety resulting in crosslinking.

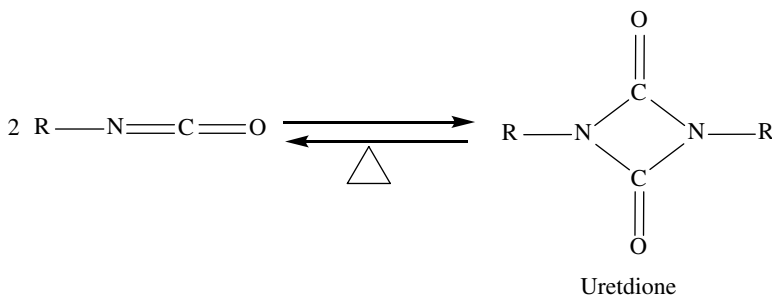


FIGURE 3.16 Dimerization of isocyanate to form uretidione.

3.3.5 Formation of Carbodiimide

Carbodiimide is formed by a catalyzed irreversible dimerization reaction of isocyanate [67, 68]. It has significant practical utility since it can be used to oligomerize 4,4' MDI; it has found numerous applications including manufacture of cast elastomers, foams, and for making composite laminates. In its simplest expression, its formation is described by Figure 3.17. Polymers formed from carbodiimides can exhibit greater flexibility and less friability versus analogous polymers synthesized from conventional diisocyanates.

Various descriptions and catalytic mechanisms have been put forward to explain the evolution of reactants to products (Fig. 3.18). Significant progress was made with the advent of phospholene oxide catalysts that are highly efficient at forming carbodiimide while minimizing the formation of other products. The carbodiimide is detectable by infrared spectroscopy by the characteristic $\text{N}=\text{C}=\text{N}$ absorption at 2140 cm^{-1} but may exhibit partial overlap with the isocyanate resonance at 2270 cm^{-1} . Another practical aspect of the formation of carbodiimide results from its unintentional formation in a closed volume (i.e., in a drum for instance) with the concomitant evolution of CO_2 resulting in an explosion hazard from pressure buildup.

Carbodiimide chemistry is also notable as part of urethane degradation pathways [71, 72]. When urethanes are heated to high temperatures (ca. $240\text{--}270^\circ\text{C}$) for extended periods of time in an FTIR cell, the characteristic carbodiimide resonance will appear at 2140 cm^{-1} . It was subsequently noticed that the carbodiimide concentration initially increased and subsequently reached an equilibrium concentration. Evolution of isocyanate was also observed but declined with time as did the urethane associated carbonyls between 1715 and 1730 cm^{-1} coupled with the growth of carbonyl resonance between 1700 and 1710 cm^{-1} . The overlap between the trimer resonance and the urethane resonance makes assignment of carbodiimide trimerization somewhat imprecise, and there is no available mass spectral data. However, the crosslinked behavior of the heated material was noted. It has been postulated that carbodiimide (which clearly forms) is capable of trimerizing according to the reaction given in Fig. 3.19. Additionally, the reaction of two isocyanates and one carbodiimide was also postulated (Fig. 3.20).

3.3.6 Formation of Uretonimine

In the presence of excess isocyanate, a carbodiimide can react reversibly to form uretonimine [73]. The uretonimine adduct is of practical importance within polyurethane technology because it results in a low-viscosity room temperature liquid [74]. The modification is accomplished by initially forming the carbodiimide with catalyst

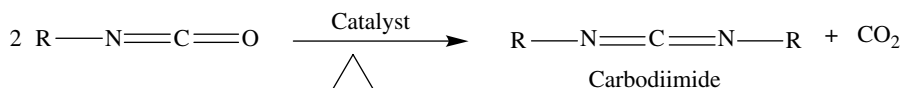


FIGURE 3.17 Catalyzed dimerization of isocyanate to form carbodiimide.

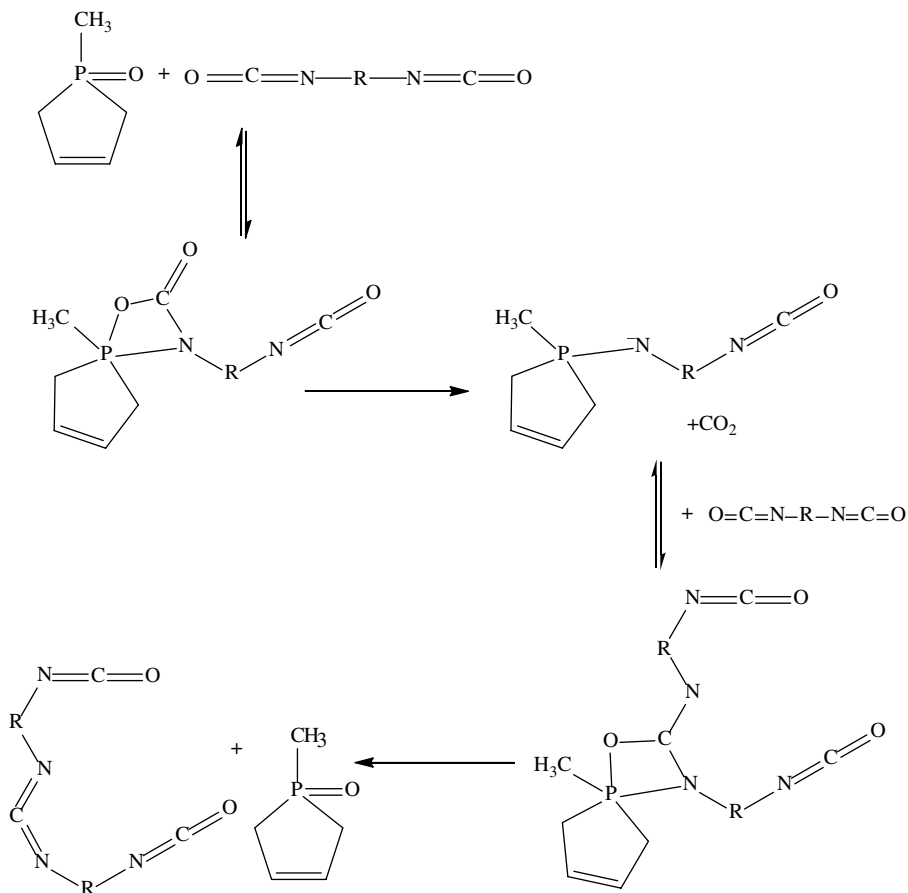


FIGURE 3.18 Phospholene catalyzed formation of carbodiimide [69, 70].

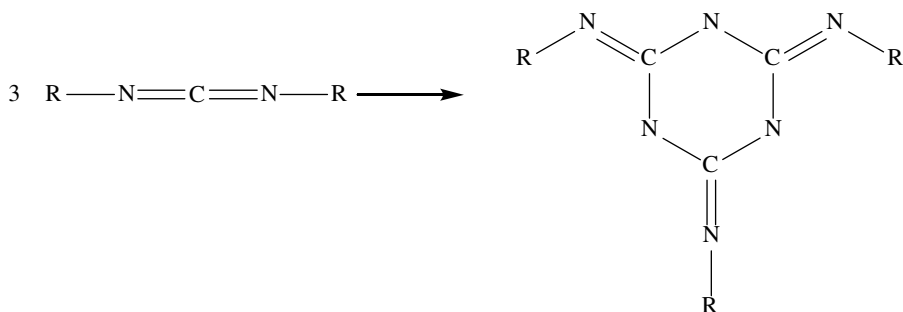


FIGURE 3.19 Proposed trimerization of carbodiimide occurring during high temperature decomposition.

at approximately 100 °C. The phospholene catalyst is subsequently neutralized (with an organic acid chloride for instance). The uretonimine forms upon cooling (Fig. 3.21). Subsequent heating to approximately 200 °C dissociates the uretonimine back to carbodiimide and isocyanate. At 200 °C, the dissociation/formation rate constant ratio has been reported to be 1.63 [75].

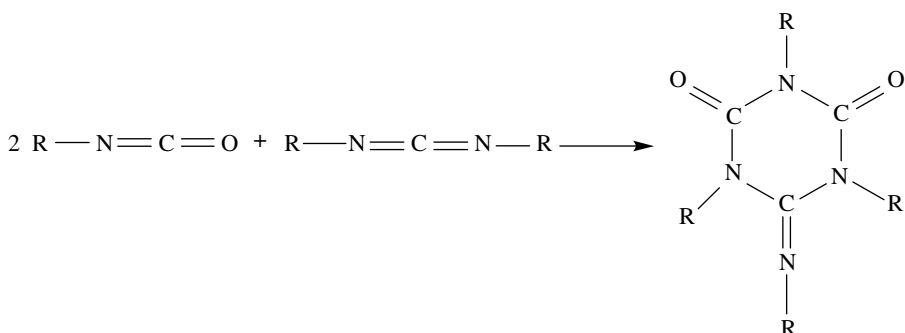


FIGURE 3.20 Proposed reaction of carbodiimide to form six-member ring during high temperature decomposition.

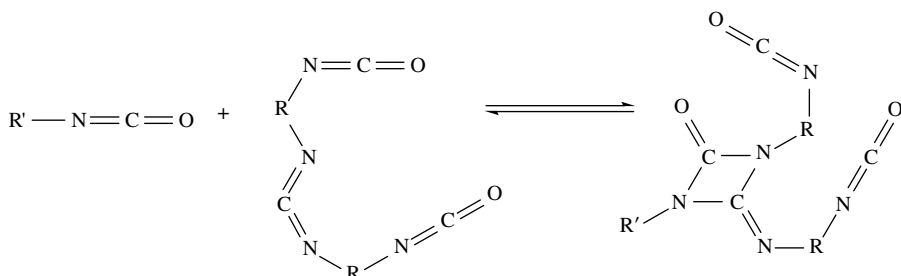


FIGURE 3.21 Reaction of carbodiimide and isocyanate to form the industrially important uretonimine.

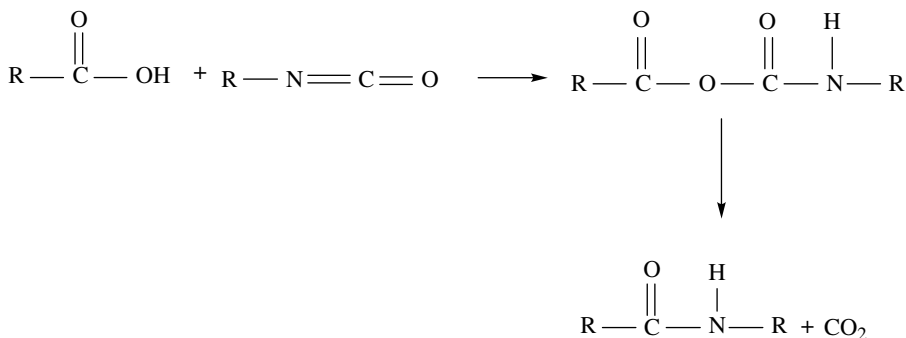


FIGURE 3.22 Reaction of aliphatic isocyanate and carboxylic acid to form the intermediate anhydride and the final amide.

3.3.7 Formation of Amides

The reaction of isocyanates and carboxylic acids has been reported in the literature, but its practical application has not yet been appreciated [76–80]. Commodity aromatic isocyanates such as MDI and TDI do not form amides with carboxylic acids, and instead reportedly form urea bonds. Aromatic isocyanates with strong electron-withdrawing groups such as cyano-, nitro-, and trifluoromethyl can result in the formation of amides in reaction with carboxylic acids. Alternatively, aliphatic isocyanates react readily with carboxylic acids in solvent to form amides according to Figure 3.22. In some cases, the anhydride is isolated, and in others, the anhydride proceeds immediately to form amide. The reaction of carboxylic acid with a dimethylpyrazole blocked isocyanate, and a magnesium triflate catalyst reportedly results in 100% amide yield in the presence of chloroform. While no mechanism for the isocyanate/carboxylic acid reaction has been reported, it has been determined that the carbon dioxide carbon originates from the isocyanate carbon.

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4

THEORETICAL CONCEPTS AND TECHNIQUES IN POLYURETHANE SCIENCE

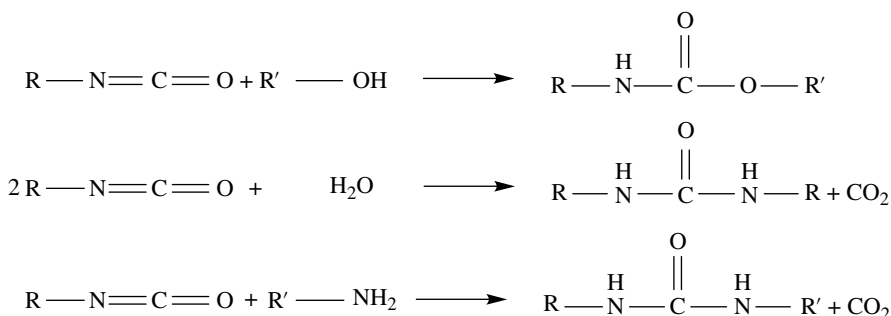
There is very good physical understanding behind polyurethane structure, properties, and the chemical processes leading to material properties. Perhaps unique among modern polymers, theoretical understanding of polyurethanes has had to await developments in different fields of materials science. Theoreticians then applied those developments to polyurethanes, almost as an afterthought. Thus, modern polyurethane science has dined well at the theoretician's table serving other materials such as composites, polymer blends, and block copolymers. Even as our *qualitative* appreciation of polyurethanes has grown very rapidly, so has understanding that some aspects of *quantitative* understanding are limited due to potentially uncontrolled parameters of polyurethane polymerization. These uncontrolled variables can have very significant effects on final polymer structure and properties. Thus, theoretical foundations of polyurethane science are sound and predictive; however, they do not as yet allow one to know ahead of an experiment if one of myriad influences on polymerization will invalidate a predicted result. Current theory allows one to look back after materials analysis and make sense of the result but not predict ahead of time if that particular result will occur.

The purpose of this chapter will not be to *derive* the equations that are currently well applied to polyurethane science. Instead the basis for those equations and their physical meaning and limitations will be presented. An intuitive understanding of the equations and their extension to predicting polyurethane performance will also be provided. The best understanding of polyurethane structure comes from a simultaneous appreciation of the thermodynamic concepts underpinning the drive from

reactants to final polymer structure coupled with the micromechanical models that allow estimation of properties from that structure. Tensile properties of elastomers can be predicted applying micromechanical results to calculations with assumptions of polymer extensibility. Bulk polymer structure can also be propagated into foam properties assuming well-known relationships associated with properties as a function of bulk density and cell structure.

4.1 FORMATION OF POLYURETHANE STRUCTURE

The chemical reactions that lead from reactants (isocyanates, chain extenders, polyols) to polyurethane polymer have been covered in detail in Chapter 3. The hard segment blocks are a result of isocyanate-chain extender reactions. The chain extender can be low-molecular weight polyols, polyamines, or water.



The first and third reactions are first order in each reactant, while the second reaction is first order in water and second order in isocyanate. Each reaction has a rate constant characteristic of the particular reactants and mutual solubilities which evolve as the reaction proceeds and heat of reaction is released. Soft segments are typically low polydispersity polyalkylene glycols ($M_w/M_n \sim 1$) or polyesters of polydispersity of about 2.0 made separately from the polyurethane polymerization.

It has been proposed that polyurethane structure from these reactions results in a block copolymer (Fig. 4.1) which can be treated using models for block copolymers [1–3] derived for well characterized or ideal block copolymer structures [4–7]. Structures developed from a basis of ideal conditions usually begin from assumptions that the structure under consideration is fully phase separated and at a point of lowest free energy. Furthermore, these thermodynamic structures are often comprised of polymers having ideal polydispersity (i.e., $M_w/M_n = 1$) in their molecular weight as well in block size.

Addition polymers such as polyurethanes can never have these attributes and by nature of their chain growth process will have polydispersities from about 2.0 to the undefined dispersity of a thermoset. This issue of nonideal polydispersity of polyurethanes versus that employed to simplify theoretical calculation should not deter us,

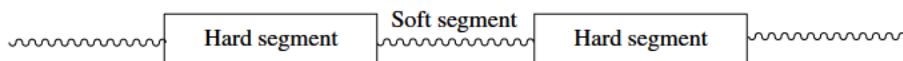


FIGURE 4.1 Hard and soft polyurethane segments make for a multi-block copolymer.

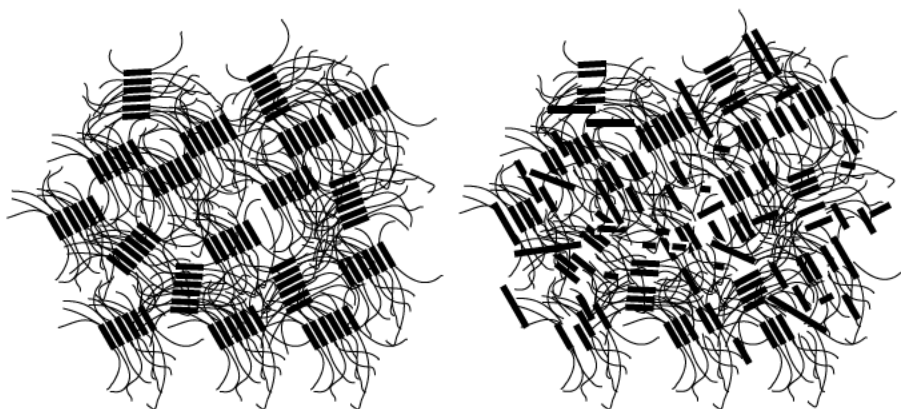


FIGURE 4.2 Representations of polyurethane final structures. On the left is an idealized structure showing monodisperse hard segment lengths and block sizes isotropically dispersed in a monodisperse soft segment. On the right is a more realistic representation showing polydisperse hard segment lengths and block sizes, along with unassociated hard segments dissolved in the soft segment.

however, since the effect of polydispersity can be anticipated and should not deny us the insights such an analysis can provide. An additional problem is the equilibrium assumption which means that there is an expectation that the theoretical analysis is performed on a structure that is in the lowest energy state. Actual polyurethane structure reflects the thermodynamics of the polymer chains coming to an equilibrium structure convoluted with the kinetic limitations of a system that may be coming to a non-equilibrium state as a result of a cooling rate that is not infinitely slow (Fig. 4.2). Again, such considerations will apply to all real block copolymers that phase separate either upon cooling from a melt or assembling from a dilute condition. These variances of polyurethane reality from model assumptions should not prevent us from obtaining a good qualitative understanding of our systems both in how close or how far they lie from ideal expectations.

Figure 4.2 expresses final conditions in which hard segment is separated or partially phase separated from the soft segment. However, the path from the initial conditions to a final state represented by Figure 4.2 is dependent on several factors including the thermodynamic incompatibility of the hard and soft phases. Analysis of phase separation in block copolymer systems can be treated in limits of very strong phase segregation [5] or weaker phase separation [4, 6, 7]. The strong and weak limits are essentially indications of how much the phases mix even when they have achieved a phase-separated state such that each phase has more (weak segregation)

or less (strong segregation) solubility in the other phase at equilibrium. Closer to the case for polyurethanes, Benoit and Hadjiaouannou [7] covered the case for block copolymers that are multiblock rather than simple diblock or triblock copolymers for instance. This matches polyurethanes in that over the course of a typical polymer chain, there may be many runs of hard and soft segment in sequence. Also cogent to polyurethane discussion is the work of Fredrickson and Helfand [6] in which polydispersity of molecular weights is included. A more recent treatment by Ginzburg et al. [8] has considered the structures created under moderate phase separation relevant to polyurethanes. In a situation of strong phase separation, the interfacial thickness between phases (see Section 5.2.3.2) is much less than the spacing between phase periodicity.

The force driving phase separation is phase incompatibility [9]. The usual case is for two blended polymers to phase separate into macrophase-separated structures. A typical macrophase-separated structure between two immiscible polymers (in this case polydimethylsiloxane and polymethylmethacrylate) is shown in Figure 4.3.

However, in the case of block copolymers such as polyurethanes, such a macrophase separation does not usually occur since the chemically incompatible sequences are confined by their covalent connections as illustrated in Figure 4.1. The result is that phase separation is on a much finer scale and interphase adhesion is complete. Structures that form from block copolymers still reflect phase incompatibility but at the same time are highly influenced by the forced intimacy of the phases [11]. This can result in a new menu of structures such as the one shown in Figure 4.4.

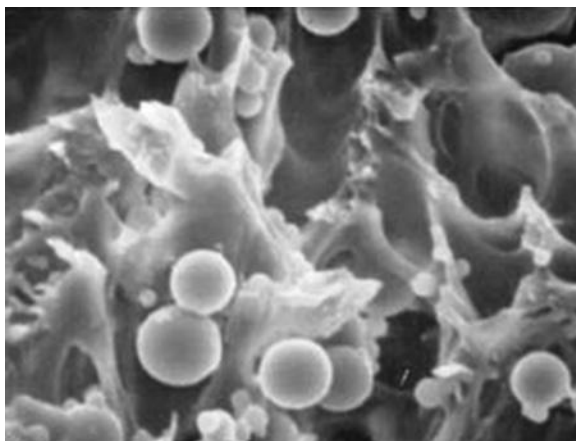


FIGURE 4.3 Scanning electron micrograph of a 20/80% (w/w) blend of crosslinked polydimethyl siloxane in polymethyl methacrylate showing macrophase separation and minimization of interfacial surface area. Full scale = 100 μm . Reprinted with permission from Ref. [10]. © Elsevier Pub.

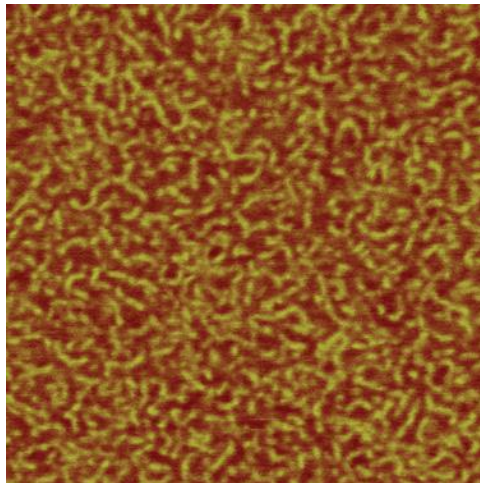


FIGURE 4.4 Tapping mode atomic force microscopy (AFM) of a TPU comprised of 40% hard 4,4' methylene diphenyldiisocyanate hydroquinone dietherethanol (MDI-HQEE) and polycaprolactone. Structure shows a cylindrical structure with no obvious orientational ordering. Full scale = 500 nm.

The incompatibility is reflected in the Flory interaction parameter (conventionally denoted by the Greek letter χ (chi)):

$$\chi_{AB} = v_{\text{ref}} \frac{(\delta_A - \delta_B)^2}{RT} \quad (4.1)$$

In Equation 4.1 v_{ref} is a reference volume that can represent a monomer unit such as that for PO ($58 \text{ cm}^3/\text{mol}$) while δ is a solubility parameter (sometimes called the Hildebrand solubility parameter or the van Krevelen solubility parameter). The solubility parameter is a measure of a material's ability to interact with another. Two materials with similar solubility parameter will be able to interact or mix, while those with different solubility parameters will phase separate. δ is calculated from the cohesive energy density that is a measure of the energy needed to remove a unit of molecules from the molecules surrounding them. Equation 4.1 can then be rewritten as

$$\chi_{AB} = v_{\text{ref}} \frac{(\sqrt{E_{\text{coh}_A}} - \sqrt{E_{\text{coh}_B}})^2}{RT} \quad (4.2)$$

Cohesive energy densities can be simply calculated using group additivity relationships provided in several well-known references [12, 13]. Polymer phase separation is strongly driven by the repulsion of unlike sequences even when the solubility parameters of the monomers of each sequence are relatively close. This is a result of

the very unfavorable enthalpy of mixing different polymer phases resulting in the driving force of polymer or block phase separation being driven by χ^N where N is the number of repeat units in the polymer chain or in the block sequence. Despite the block repulsion which in the case of polyurethanes can begin at quite low N values [3, 14], the effect of the forced intimacy of the blocks resulting from their covalent attachments is to potentially produce periodic structure such as shown in Figure 4.4. The structures that form will be a result of the block incompatibility, the volume fraction of the blocks, and often processing conditions which can greatly complicate a priori quantitative prediction of final structure [15]. When homopolymers phase separate, they are usually observed to minimize their interfacial surface area as seen in Figure 4.3. When block copolymers phase separate, they may form spherical structures, but they may also form alternative structures such as elongated cylinders shown in Figure 4.4, spherical structures such as observed in Figure 5.6b, or lamellar structures as shown in Figures 5.6a and 4.5. In limited cases, a gyroid structure such as Figure 5.9 may be observed (Table 4.1).

Figures 4.4 and 4.5 point out the very important role that the relative phase volumes play in the final phase-separated polyurethane structure.

Theoretical treatments of microphase separation transitions such as illustrated by Figures 4.4 and 4.5 result in phase diagrams typified by Figure 4.6. The boundaries indicate the combined effects of incompatibility and molecular weight (i.e., χ^N) on phase separation and structures. The equation by which the phase boundaries are computed is as follows.

$$\chi^N = (\chi^N)_o \frac{1}{1 - (0.25 - f_i)(1 - f_i)/0.25 - \alpha_i)} \quad (4.3)$$

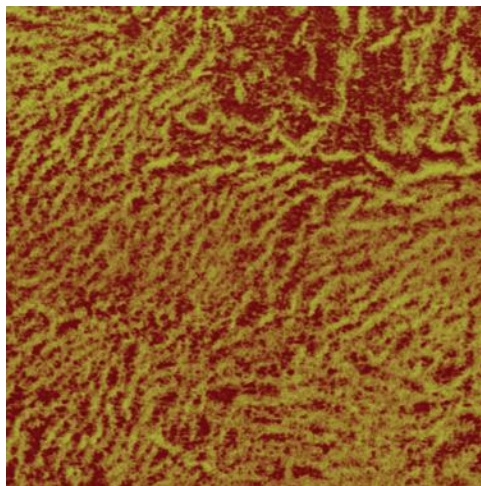


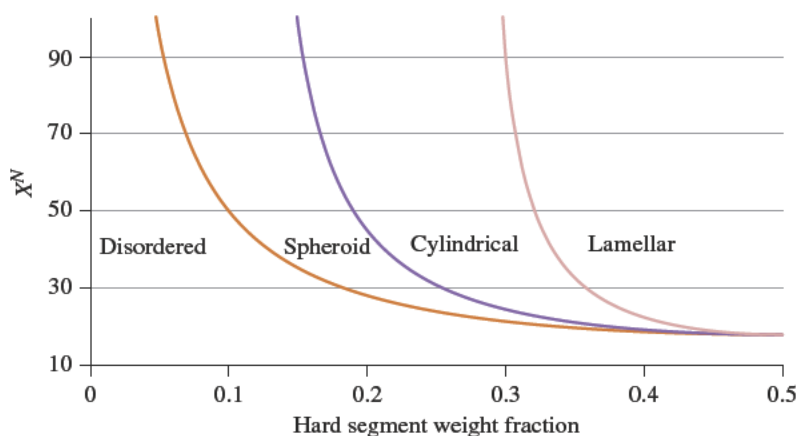
FIGURE 4.5 Polyurethane elastomer of the same composition as the polyurethane in Figure 4.4 except having 45% hard segment. Full scale is 1 μm .

TABLE 4.1 Examples of solubility parameters calculated by the method of Bicerano^a

Polymers	Solubility parameter $\frac{\text{cal}^{1/2}}{\text{cm}^{3/2}}$
Polyethylene oxide	8.8
Polypropylene oxide	8.5
Polytetramethylene glycol (PTMEG)	8.8
Polycaprolactone	8.3
Seed oil derived polyol	7.6
MDI-BDO	11.2
IPDI-BDO	10.38
MDI-diethyltoluenediamine	12.2
TDI-water	14.1
MDI-water	10.7

To convert to $\text{Pa}^{1/2}$ multiply by 2.045.

^aRef. [13].

**FIGURE 4.6** Illustrative phase diagram of a polyurethane capable of exhibiting different phase structures as a function of hard segment volume or molecular weight.

The details of this equation are reasonably straightforward but mask a very sophisticated derivation and line of reasoning [8]. The value $(\chi^N)_0$ is the value of χ^N below which there will be no phase separation. In Figure 4.6, it is approximately 18. This value is particular for polyurethanes and is the limit below which all phase boundaries converge to a disordered phase. The value of 10.495 has been calculated for χ^N representing infinite molecular weight diblock copolymers. The effect of the finite and polydisperse molecular weight of polyurethanes and their multiblock structure is to increase χ^N_0 [6, 7]. This is equivalent to a suggestion that for multiblock and polydisperse block, and crosslinked copolymers such as a polyurethane, a higher level of phase incompatibility

is required to obtain structured phases. Alternatively, it could be interpreted that for a block copolymer such as a polyurethane, a disordered phase can be obtained upon heating to a lower temperature than an ideal diblock of infinite molecular weight. In other words, one must cool from a melt to a lower temperature to obtain microphase separation. The constant 0.25 is calculated from the expression $f_i(1-f_i)$ for the value above which one would expect a phase inversion. In the illustrative case depicted in Figure 4.6, phase inversion occurs at a hard segment fraction (f) greater than 0.5. It can also be intuitively thought of as the ratio of the two blocks in any single chain. The term α_i represents the evaluation (calculated, measured, or guessed) for $f_i(1-f_i)$ resulting in a phase boundary for a particular morphology i . Thus in Figure 4.6, the phase boundary for the disordered/spherical transition is calculated with $\alpha_i=0$, for the spherical to cylindrical phase transition $\alpha_i=0.098$ and for the cylindrical to lamellar transition $\alpha_i=0.206$. Conditions in which multiple phases can be simultaneously observed have been treated as a special case for the common occurrence where mixing of reactants is nonideal or the hard segment fractions are very close to the phase boundaries and statistical fluctuations may result in phase diversity. The means by which these phases form from the melt and affect properties is discussed in the following.

The phase separation mechanism by which phase morphologies (Fig. 4.6) can occur has been reviewed and has been validated experimentally for polyurethanes [16–19]. Since polyurethane is simultaneously forming, phase separating, and potentially creating a gaseous coproduct, the path from high temperature melt to final product is quite a bit more complicated than that for an ideal block copolymer. For example, considerations of *ideal* block copolymers are that as the melt cools (quenches), the overall system free energy is at a minimum at each temperature arriving at a final equilibrium structure at the final state. The depth of quench is sometime referred to as the difference between the upper critical solution temperature and the system temperature [20]. In reactive systems like polyurethanes, the system is evolving both chemically and rheologically, changing the definition of equilibrium conditions continuously (i.e., there is no reference state). Furthermore, as the reactions proceed and oligomers of hard segment coupled to soft segment form, they can act as surfactants with the resulting change in the distribution of χ values and the interfacial energy of components in the mixture. In this case, the quench is potentially determined by temperature and simultaneously by the degree of conversion to polymer. As the polymer is forming and the block repulsions are initiating phase separation, the phases may separate by either nucleation and growth or by spinodal decomposition.

The difference between nucleation and growth and spinodal phase separation mechanisms is critical to understanding final polymer morphologies and controlling properties via formulation and processing [18, 19]. In a phase separation by nucleation and growth, the sample is quenched to a state where the solubility of each pure phase of the block exceeds the capacity of the melt. The phase separation begins as the homogeneous mixture enters this unstable region of the phase diagram (Fig. 4.7). Nucleation and growth is the expected mechanism when the system temperature proceeds slowly to the binodal curve [21]. The composition of the phase-separated region proceeds along the arms of the binodal (or coexistence) curves to a composition

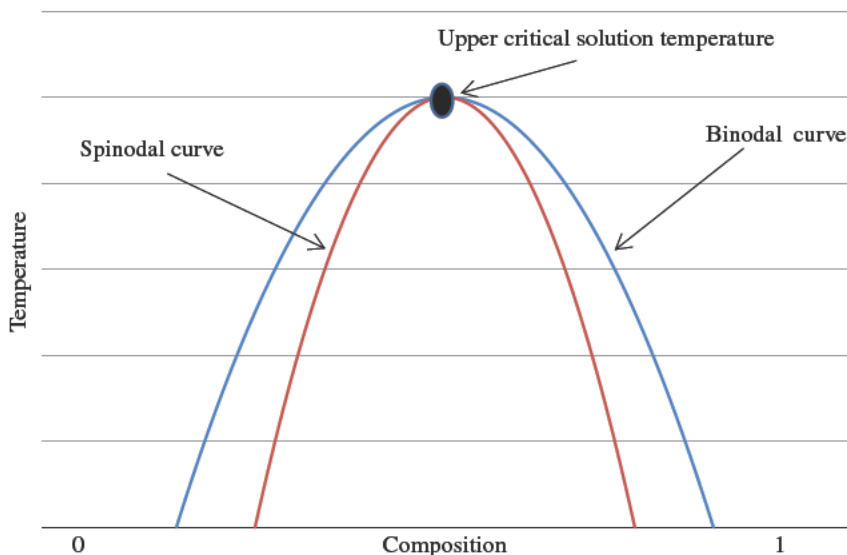


FIGURE 4.7 The case for polyurethanes is decomposition through the upper critical solution temperature upon temperature decrease or molecular weight increase.

of two major phases, each one solubilizing the minor component at the solubility limit of the other phase [22]. Nucleation occurs since in this mechanism dispersed nuclei of each phase will form in the melt as the activation energy for nuclei formation exceeds the free energy of surface formation [23, 24]. Radiation scattering such as small angle x-ray scattering (Section 5.2.3.2) from a system phase separating by a nucleation and growth mechanism will exhibit a linear decrease with scattering angle and increase with time at a fixed angle according to Equation 4.4.

$$I = K (t - \tau)^n \quad (4.4)$$

Time lag prior to the inception of nucleation, τ , is often arbitrarily made zero. The value n for nucleation and growth is well established to be between 3 and 4 such that a plot of log intensity increase with log time at a fixed angle will have a slope between 3 and 4. This behavior is strong evidence for a nucleation and growth mechanism of phase separation.

In the case of spinodal phase decomposition, the system is rapidly quenched (i.e., cooled rapidly or made unstable by rapid molecular weight growth) and the system will occupy an unstable position bounded by the spinodal curve of Figure 4.7. In this case, phase separation will initiate through the existing concentration fluctuations with increasing amplitude and with a characteristic interphase spacing. The separating phases will form two co-continuous and sometimes inter-penetrating structures [20, 25–27]. In some cases, the final morphology may assume the appearance of a structure developed by nucleation and growth due to phase coalescence and coarsening at

long times. However, the difference in mechanism as measured by radiation scattering is diagnostic. In a spinodal decomposition, the system may exhibit a time lag in the development of structure; however, once phase separation begins, intensity will grow at a characteristic angle which can be translated via the Bragg equation (5.6) into a characteristic spacing. The scattering intensity will have a finite breadth reflecting inhomogeneity of the periodicity within the sampled volume, but the maximum will be at constant angle and will exhibit exponential growth according to Equation 4.5 where $R(q)$ is the amplitude growth rate of fluctuations of wave number q .

$$I(q,t) = I(q,0)e^{[2R(q)t]} \quad (4.5)$$

Thus a plot of $\ln I(q,t)$ versus time (t) should yield a straight line during the early stages of phase separation. While there is no question that the reaction-induced phase separation that occurs during polyurethane polymerization is different from the thermally induced phase separation upon cooling the melt of an ideal block copolymer, the behavior of polyurethane foam during foam formation exhibits scattering behavior consistent with a spinodal mechanism for phase separation. In the case of thermoplastic elastomers, the resulting structure can be consistent with either mechanism of phase separation. Specific elastomer processes can certainly exhibit the appearance of a phase separation that has developed via nucleation and growth (Fig. 4.8) using a slow cooling process, and also scattering signatures not confirming

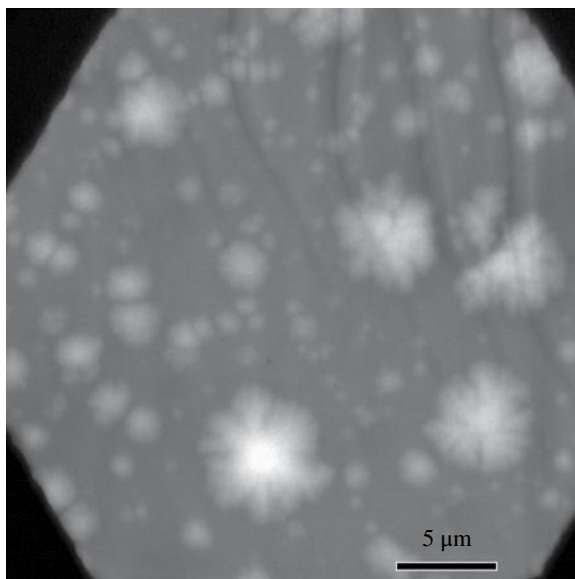


FIGURE 4.8 TEM of a cast polyurethane elastomer with 35% 4,4' methylene diphenyldiisocyanate 1,4 butanediol (MDI-BDO) hard segment with spherulitic appearance typical of a nucleation and growth phase separation. Polymer was formed at 85°C and sat quiescently at temperature for 4 h.

spinodal decomposition using a fast reactive injection molding process [18]. Many other thermoplastic polyurethanes (TPU) elastomers will exhibit finely divided co-continuous gross morphologies typical of spinodal decomposition [17].

The significant differences in appearance observed between a morphology from spinodal and nucleation and growth mechanisms are a result of the difference in details of the mechanism. In both mechanisms, the individual blocks of an A-B block copolymer will possess some level of mutual insolubility and solubility in the melt. As the blocks diffuse, the local concentrations of components will exhibit increasing fluctuations. Fick's law stipulates that flux of an ideal mixture will be proportional to a concentration gradient.

$$J_{A,B} = - \frac{D_{A,B} C_{A,B}}{RT} \frac{\partial \mu_{A,B}}{\partial C_{A,B}} \quad (4.6)$$

For nonideal mixtures or solutions, the driving force is the gradient of chemical potential.

$$J_{A,B} = - \frac{D_{A,B} C_{A,B}}{RT} \frac{\partial \mu_{A,B}}{\partial x_{A,B}} \quad (4.7)$$

In Equations 4.6 and 4.7, D is the diffusion coefficient proportional to the squared velocity of the diffusing particles depending on temperature, viscosity of the surrounding medium, and the size and shape of the diffusing block, and C is the concentration of the individual species.

If the value of $\partial \mu_{A,B} / \partial C_{A,B}$ is positive, then the diffusion coefficient is positive and diffusion occurs in the direction from high concentration to lower concentration as usually observed. When $\partial \mu_{A,B} / \partial C_{A,B}$ is negative, then the direction of diffusion is from lower concentration to higher concentration. The former case is typical of diffusion occurring in a nucleation and growth mechanism [28, 29]. This is because the interface between two phases growing along the binodal curve is “infinitely” sharp and so the concentration just outside this phase is quite low, and away from the growing separating phase, the concentration of species is relatively higher. The latter case is typical of phase growth by a spinodal mechanism. This is because the phase formed via spinodal separation is not sharp and the concentration between concentration fluctuation waves is relatively lower between the concentration wave peaks yet still diffuses in the direction of the higher concentration peaks. In some cases and at long times, the morphology created by a spinodal decomposition and nucleation and growth mechanism can be indistinguishable due to coarsening (“Ostwald ripening”) of the spinodal phase structure with time.

4.2 PROPERTIES OF POLYURETHANES

Modern understanding of polyurethane structure–property relationships is conventionally first associated with the work of Cooper and Tabolsky in 1966 [1]. Their recognition that modulus values of TPU could not be modeled using standard

equations for filler reinforcement led to detailed understanding of these materials. Greater theoretical insight awaited further experimental progress. Koberstein and Stein [3] suggested that phase separation of a reactive block copolymer system such as polyurethane occurs only after the attainment of a critical hard segment length (or average number of repeat units). Consistent with the conclusion of Cooper and Tablosky, they ruled out a random two-phase morphology on the basis of their X-ray scattering curves. They estimated a critical hard segment length of between 2 and 3 depending on numerous hard segment and processing factors. Subsequent work by Ryan et al. [9] suggested a minimum critical length slightly lower than this.

With experimental description of the polyurethane structure at many length scales, and theoretical formalisms of polymer superstructure from block-copolymer theories, composite models were developed that could account for the properties of polyurethane foams and elastomers. Block copolymer theory (see Section 4.1) had suggested that block copolymers could arrange themselves into spherical, cylindrical, lamellar, and gyroid structures, for instance, and various microscopy techniques were enlisted to detect morphologies that were forming during reactive polyurethane processing. In fact many block copolymer structures that can be observed have indeed been observed in polyurethanes. Spherical (Fig. 4.8), cylindrical (Fig. 4.4), and lamellar (Fig. 4.5) morphologies have been observed by the author and others [15, 30]. Gyroid-like morphologies are also observable (see Fig. 5.9). What has not been observed is ordered packing of the hard segment phases such as is observed in ideal block copolymers. Thus cylindrical hard segment phases can be observed, but hexagonal packing of those cylinders for instance is not.

Regardless of the phase separation temperature or molecular weight, the calculation of properties based for a specific structure are significantly affected by the assumptions made in the composite model. Simple equations can result from sophisticated analyses and subtle assumptions.

4.2.1 Models and Calculations for Polymer Modulus

An example of a relatively simple equation for a two-phase composite model that has been employed to model polyurethane properties is the Kerner equation [31]. Like many such equations, the derivation of the final equation assumes a macroscopically homogeneous and isotropic solid with properties defined by the properties and concentrations of the components in the bulk. One component is assumed to be on average spherical and randomly distributed within a uniform matrix. Key considerations in this model are that the composite inclusions are bonded to the matrix and—they are isolated from each other—thus, they do not form a co-continuous structure within the composite. The approach used by Kerner is termed a generalized self-consistent field approach. Kerner assumed that the spherical particle is embedded in a spherical shell of matrix surrounded by an “infinite” body with the average composite properties. A basis for the equation is also that the adhesion between the filler and the matrix is perfect, so that displacements across boundaries are continuous and invariant. The spatially averaged properties of the embedded particle must match the properties of the matrix. Analysis of the cell and its properties and distributions are

iterated until there is a match between the modeled volume element and the bulk reference [32]. The resulting Kerner equation is given by Equation 4.8 where G_c is the shear modulus of the composite, G_p the shear modulus of the matrix phase, G_f the shear modulus of the filler phase, v_p and v_f are the volume fraction of polymer and filler respectively, and ν the Poisson's ratio.

$$\frac{G_c}{G_p} = \frac{(G_f v_f) / \left[\left[(7-5\nu) G_p + (8-10\nu) G_f \right] \right] + (v_p) / \left[\left[15(1-\nu) \right] \right]}{(G_p v_f) / \left[\left[(7-5\nu) G_p + (8-10\nu) G_f \right] \right] + (v_p) / \left[\left[15(1-\nu) \right] \right]} \quad (4.8)$$

The form of Equation 4.8 is the same as the Clausius–Mossotti equation for defining the properties of two-component systems, each component having definable and unique properties [33]. The terms $G_f(7-5\nu)/(8-10\nu)$ are derived for the purpose of setting upper and lower bounds on the bulk moduli [34]. The value of the Poisson's ratio, ν , will have a quantitative effect on the result, but not a qualitative effect. In principle, ν should be a function of the filler volume fraction for the usual case that the matrix and the filler have different Poisson's ratio values, but in practice this is usually not a significant effect.

In contrast to the isolated particle assumption of Kerner's equation 4.8, the Davies equation 4.9 assumes that the filler phase and the matrix phases are co-continuous and adhesion between the phases is perfect [35]. Other than the co-continuity assumption, the physical foundation of Davies' model is similar to that of the Kerner equation [36]:

$$G^{1/5} = \phi_1 G_1^{1/5} + \phi_2 G_2^{1/5} \quad (4.9)$$

In Equation 4.9 ϕ_i represents the fraction of component i while G represents the respective shear modulus. The Davies equation has been used successfully to model the composition dependence of numerous two-phase systems including semi-crystalline polymers [37], block copolymers [38], and block copolymers with an interstitially polymerized third polymer phase [32, 39].

The simplicity and success of the Davies equation has inspired modifications to take account of physical phenomena associated with the phase separation process such as phase percolation associated with the transition from the spherical to the cylindrical phase transition (Fig. 4.6). An example might be typified by Equation 4.10 [38] that has demonstrated additional utility in evaluating polyurethane elastomer data.

$$G^{1/5} = \phi_p G_H^{1/5} + (1 - \phi_p) G_S^{1/5} \quad (4.10)$$

$$\phi_p = [\phi_H - \phi_{sc}]$$

In Equation 4.10, ϕ_p is the hard segment weight fraction that is reinforcing, and ϕ_{sc} is the hard segment fraction at which the phase morphology transitions from a spherical to a cylindrical phase morphology which can be interpreted as a percolation threshold.

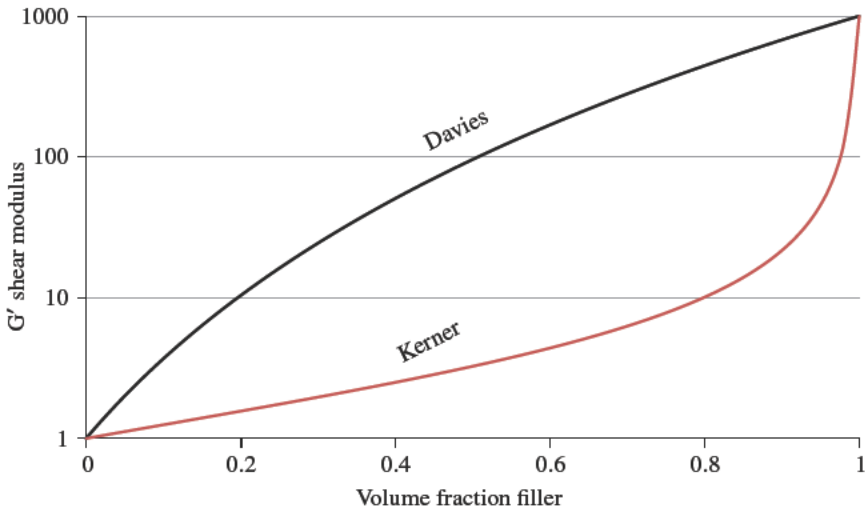


FIGURE 4.9 Graphical representations of the Kerner and Davies equations using the assumption of a 10^3 difference between filler and polymer moduli (relevant to polyurethane systems).

A visual comparison of the Davies and Kerner equations is provided in Figure 4.9. The rapid and continuous increase of modulus in the Davies equation is reflective of the percolation assumption. The slow increase in modulus observed for systems modeled by Kerner's equation reflects the noninteraction of particles and their non-continuous phase status.

Both the Davies and Kerner equations lack recognition that at some hard segment fraction there can occur a phase inversion in which the hard segment is the matrix phase and the soft segment is in effect the filler. Budiansky [40] proposed an alternative two-phase composite model that would provide a means for such inversion to occur. The Budiansky model differs fundamentally in that his model embeds the filler particle (hard segment in a polyurethane) directly into the effective medium rather than in the matrix polymer. In this manner, the physics and the equation are symmetric with replacement of matrix and filler fractions (Eq. 4.11).

$$\phi_2 = \frac{G_1 - G}{G(G_1 - G_2)} \times \left(\frac{3}{5}G + \frac{2}{5}G_2 \right) \quad (4.11)$$

In Equation 4.11, ϕ_2 is the variable volume fraction, G is the composite modulus, and G_1 and G_2 are the filler and matrix moduli. A graphical representation of the Budiansky equation is shown in Figure 4.10. This graph shows the realistic case for systems intermediate to the Kerner and Davies case in that the filler may at some range of volume fraction exists in isolated domains. In the Budiansky representation, the modulus function begins to show deviation from an initial linear increase at

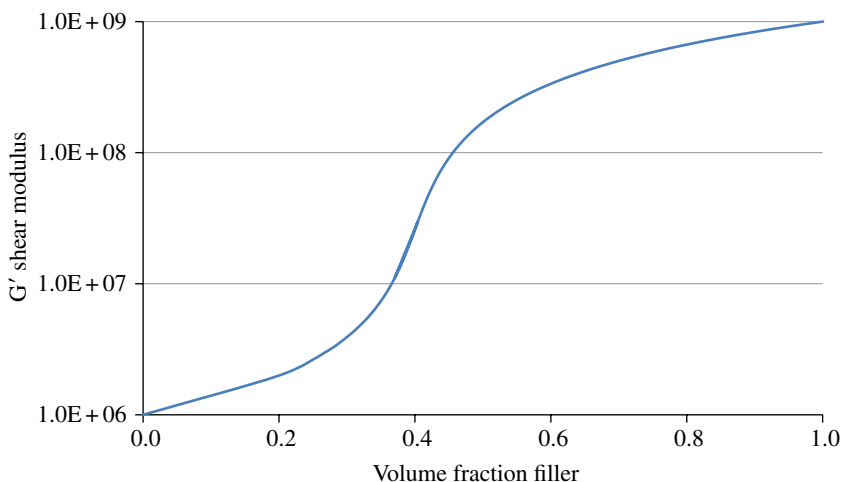


FIGURE 4.10 Graphical representation of the Budiansky equation using a soft phase modulus of 1 MPa and a hard phase modulus of 1 GPa as relevant to polyurethane systems.

approximately 30% volume percentage filler. At a volume fraction of about 60%, the function again assumes a linear increase suggesting a phase inversion has occurred. While a phase inversion is not a requirement of a specific composite system in this range, and the specific details of the derivative in any specific range may be inexact, the basic form of the Budiansky equation is quite similar to that observed in actual polyurethanes as a function of hard segment volume. The actual values obtained in the moderate to high hard segment volumes are often better approximated by the Davies equation [32, 41].

Another commonly invoked equation to predict composite modulus is the Halpin-Tsai equation (including the numerous variations and refinements that have been developed). This equation is unique in that it allows for distinction of filler shape. It has been well applied to many composite materials and materials that can be modeled as composites, extending from semi-crystalline polymers to nanocomposite filled thermosets [39, 42–45]. For polyurethanes, it is possible to use a simple form of the equation such as Equation 4.12.

$$E_{\text{composite}} = \frac{\{E_{\text{filler}} + 2A[E_{\text{filler}} + (1 - \phi)E_{\text{matrix}}]\}}{[(2A + \phi)E_{\text{matrix}} + (1 - \phi)E_{\text{filler}}]} \quad (4.12)$$

Where A is the filler aspect ratio, ϕ is the filler volume fraction, and the other symbols are the respective moduli. The aspect ratio is the ratio of the filler's length to width. Thus a spherical particle would have an aspect ratio of 1 while a fiber might have an aspect ratio of 100 or higher. An assumption of Equation 4.12 is that anisotropic fillers are perfectly aligned. The modulus for the direction perpendicular

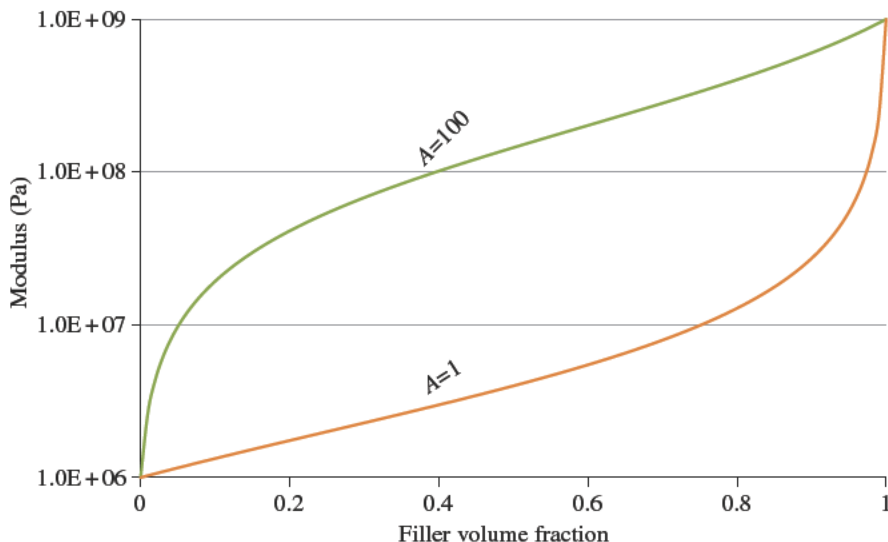


FIGURE 4.11 Graphical representation of the Halpin-Tsai equation (4.12) using a soft phase modulus of 1 MPa, a hard phase modulus of 1 GPa, and with aspect ratio (A) of either 100 or 1.

to fiber orientation can be calculated with the alternative assumption of $A = 1$ and the modulus of the overall random composite calculated by taking the average. A graphical representation of the Halpin-Tsai expression is given in Figure 4.11 showing the significant orientation effect of high aspect ratio fillers. The similarity between the Kerner result (Fig. 4.9) and the Halpin-Tsai result for $A = 1$ reflects the parallel initial assumptions.

An approximate expression (Eq. 4.13) that can also be applied is based on the expressions of Kolarik [46] and Bicerano [47] and is based on a simple percolation equation.

$$E_{\text{composite}} = E_{\text{filler}} \left(\frac{(\phi_{\text{filler}} - \phi_{\text{perc}})}{1 - \phi_{\text{perc}}} \right)^{\beta} \quad (4.13)$$

Where ϕ_{perc} is the volume fraction at which the filler percolates as a co-continuous phase. For polyurethanes, the percolation threshold can be construed at the spherical to cylindrical phase transition or even the cylindrical-to-lamellar phase transition (see Fig. 4.6). The exponent β is sometimes called the percolation exponent and is an adjustable variable on the order of 2. An obvious simplification in this calculation is the invitation to neglect the soft segment since its modulus is much smaller than that of the hard segment. The equation does not have a defined result below the percolation threshold but can be refined to compensate if desired. Results are qualitatively similar to the Davies equation (Fig. 4.12).

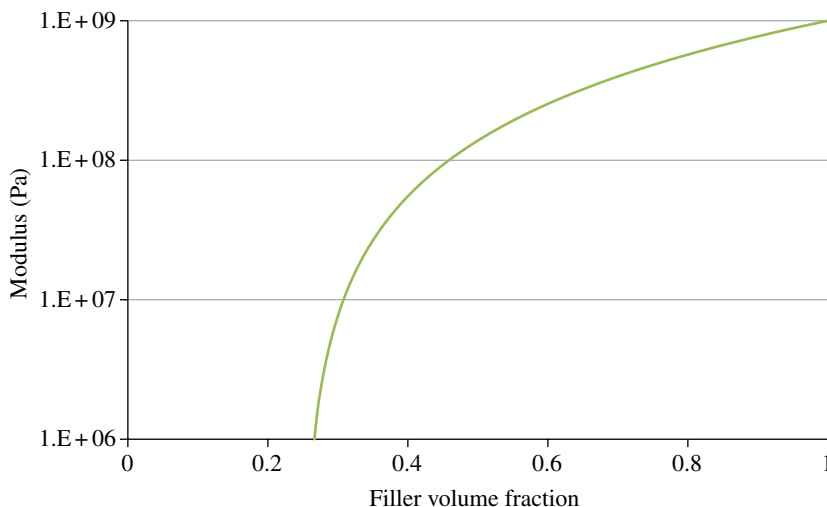


FIGURE 4.12 Graphical representation of the modulus predictions based on a percolation equation (4.13) with a filler modulus of 1 GPa and a percolation threshold of 0.25 filler volume fraction.

4.2.2 Models for Elastomer Stress Strain Properties

As discussed in Section 4.2.1, models predicting the modulus of polyurethanes have been proposed. Based on realistic models of polyurethane structure, several have been shown to reproduce measured properties with good fidelity. Part of the success of these models is that they occur in the low strain-linear response range for the materials such that there are no irreversible plastic deformations that occur during the test. Modeling the whole stress strain curve is a much larger challenge. High strain experiments on polyurethanes enter the domain of nonlinear viscoelasticity and irreversible processes that occur to the soft segment (i.e., disentanglement and bond rupture), hard segment (shear yielding and orientation), and physical processes that may be reversible, but only partially so on the time scale of the measurement (i.e., hysteresis and elastic set). To some extent, polyurethane stress-strain behavior can be anticipated based on composition, phase structure, and reasonable assumptions about how polymers behave.

4.2.2.1 Factors that Affect Polyurethane Stress-Strain Behavior For any given polyurethane sample undergoing mechanical testing, there are four scenarios that one should consider when trying to anticipate large strain behavior. These scenarios are shown schematically in Figure 4.13.

Scenario 1: Hard and soft phase are below their respective glass transition temperatures exhibiting properties of a hard glassy polymer. The plastic exhibits linear elastic behavior up until large scale flow is initiated at the yield point, accompanied by a clear necking as the material exhibits Poisson narrowing

initiating at some sample nonuniformity. The material elongates plastically up until failure which is a function of strain rate, temperature, defectivity, and details of the material structure. An example of a polyurethane sample tested within this range is shown in Figure 4.14.

1	2
Hard phase below Tg	Hard phase below Tg
Soft phase below Tg	Soft phase above Tg
3	4
Hard phase above Tg	Hard phase above Tg
Soft phase below Tg	Soft phase above Tg

FIGURE 4.13 Diagram of the categories of phase-separated polyurethanes that affect stress–strain properties apart from molecular weight.

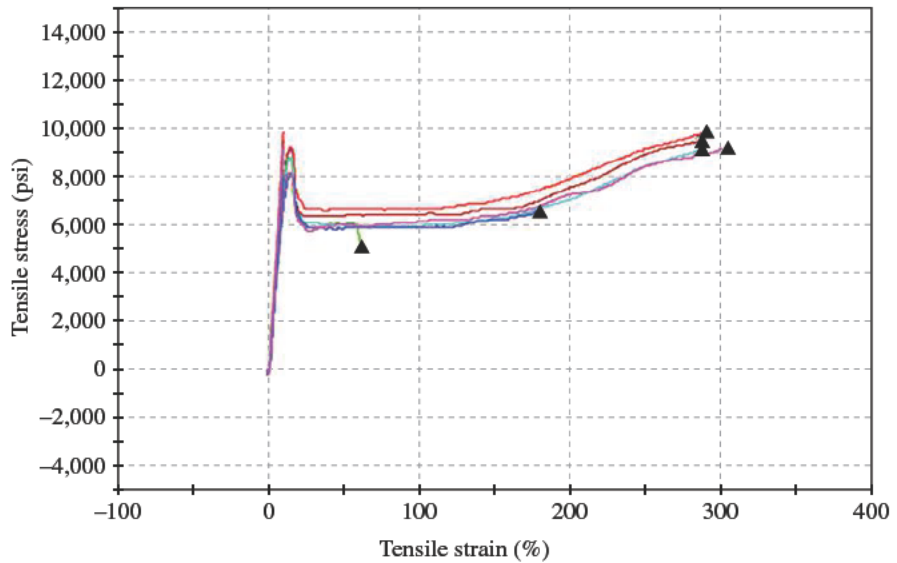


FIGURE 4.14 Illustrative stress–strain curve for a polyurethane elastomer characterized by Scenario 1 with both soft and hard segments below their glass transition temperatures. Reprinted with permission from Ref. [48]. © American Chemical Society.

Scenario 2: Hard phase is below its glass transition temperature and soft phase above its glass transition temperature. This is the typical situation for a polyurethane elastomer in application. In this case, the material strain properties will be sensitive to the microphase separation such that if the material is not microphase separated it will elongate like a crosslinked rubber (Fig. 4.15a). If the material has microphase separated but is in a spherical phase, or is a different phase below its percolation threshold, it may elongate like a filled rubber (Fig. 14.15b). If the material is phase separated and the hard phase is above its percolation threshold, the material will behave as a composite (Fig. 14.15c) having a high initial modulus that drops rapidly at elongations above a poorly defined yield type point.

Scenario 3: This is a special case that is rarely observed in practice. Such a case is conceivable in the instance where the soft segment is an aromatic polyester phase and the hard segment is comprised of an aliphatic isocyanate and a branched diol. Depending on their volume fractions, the stress-strain curves may appear as a special case of those observed in Figure 4.15.

Scenario 4: In the case, where the soft segment and the hard segment are both above their respective T_g , one should expect that the material will extend as a weakly crosslinked elastic network, elongating at relatively low stress and breaking at relatively high extensions and low stress (Fig. 14.16).

Attempts to model stress strain curves have usually followed an “Equivalent Box Model” such as employed by Kolarik [46, 49, 50] and others. This model separates the total stress into the sum of stress contained by the hard segment and a soft segment (Eq. 4.14) that may have dissolved components of hard segment in it (Fig. 4.17).

$$\sigma = \sigma_{HS} + \sigma_{SS} \quad (4.14)$$

A representation of the functional dependence of stress with strain that allows a separable and additive calculation would possibly be represented by Equation 4.15. In Equation 4.15, φ_h is the volume fraction of hard phase, ε is the strain, ε_y is the yield strain, E_h is the modulus of the hard phase (estimated from the modulus of a conventional thermoplastic below its glass transition temperature), E_s is the modulus of the soft segment, and $P(\lambda)$ is a complex function reflecting the stress amplification of the dissolved hard phase within the soft segment as it reinforces the soft segment as a function of the soft segment strain. This phenomenon of strain reinforcement was first observed as a deviation of measurements on polyurethanes from the behavior predicted by the Mooney–Rivlin equation [51]. The Mooney–Rivlin equation has been used with good success to model stress-strain behavior to moderate strain levels at which point the limited or constrained extensibility of chains becomes significant [52–54]

$$\sigma_h = \varphi_h E_h \varepsilon_y \left(1 - e^{[\varepsilon/\varepsilon_y]}\right) \quad (4.15)$$

$$P(\lambda)P(\lambda) \sigma_s = (1 - \varphi_h) E_s P(\lambda)$$

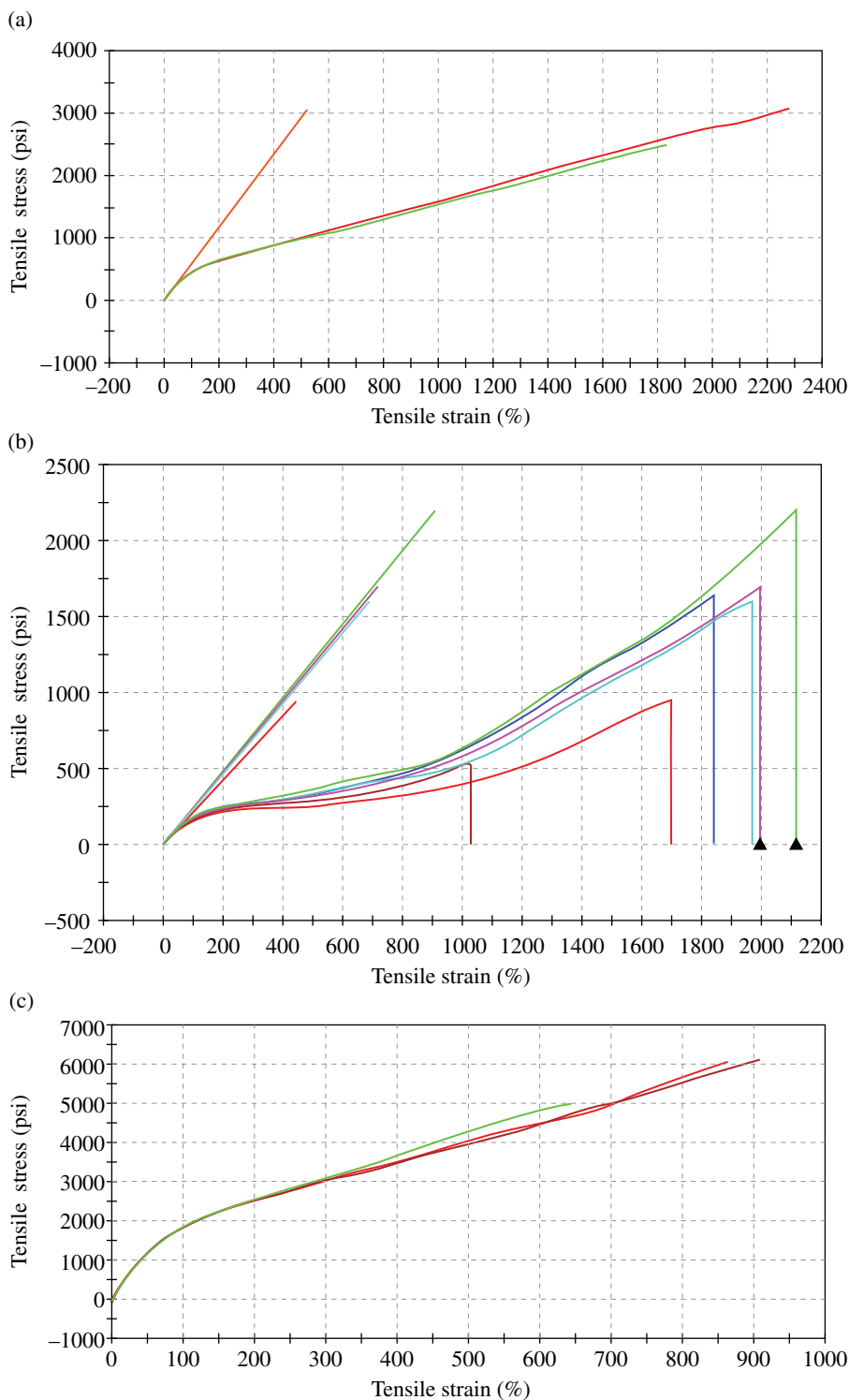


FIGURE 4.15 Illustrative stress–strain curves for a polyurethane elastomers of Scenario 2. (a) The hard phase is below the microphase separation limit, (b) the hard phase is microphase separated but not co-continuous, and (c) the hard segment is phase separated and above the percolation threshold. Reprinted with permission from Ref. [48]. © American Chemical Society.

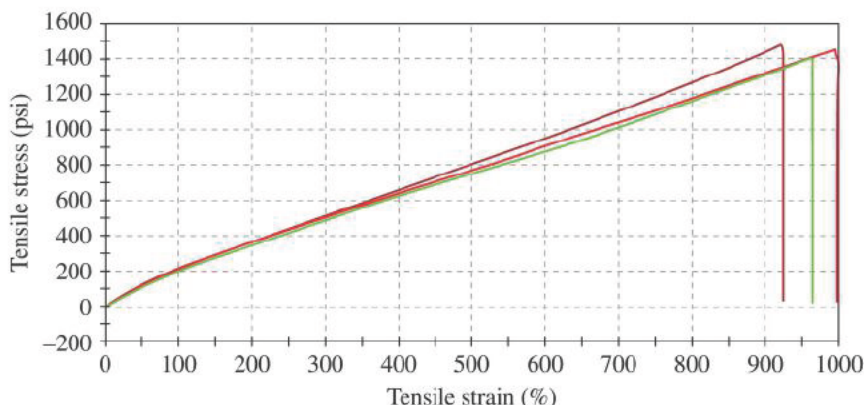


FIGURE 4.16 Illustrative stress–strain curve for a polyurethane elastomer with both the hard and soft segments above their respective glass transitions.

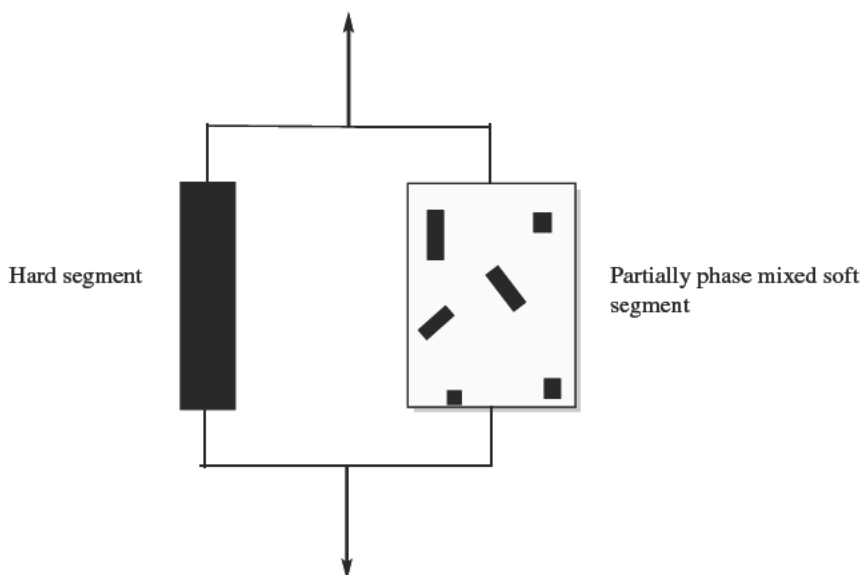


FIGURE 4.17 The Equivalent Box model for calculating large strain properties of polyurethanes.

As strain is increased, the stress amplification of dissolved hard segments decreases since some of the hard segment clusters yield. At the limit of maximum extension, when all the soft segment chains have fully extended, all or most of the hard segment clusters would have yielded prior to soft segment chains breaking, and the stress amplification of dissolved hard segment is low (assuming the dissolved cluster cohesive energy is less than the bond energy of the soft segment chain) [55, 56].

Calculation of ultimate elongation and toughness (the integral under the stress strain curve) for an unfilled Gaussian network is usually related to the contour length

of the chains at which point they are completely stretched, and incremental strain increases will result in chain breakage. For polyurethanes within Scenario 2 (Fig. 4.13), the situation is substantially more complex. Elongation of these systems is known to depend on unquantifiable factors associated with sample history and processing minutiae. Reasonable attempts have been made to model the stress–strain behavior of crosslinked glassy materials like epoxies. Predictions from semi-empirical equations (i.e., the Martin, Roth, and Stiehler equation) and an analogue equation replacing stress and strain variables with normalized failure stress and strain (Eq. 4.16) and experimental validation have been obtained [57, 58].

$$\sigma = E \left(\frac{\varepsilon}{\lambda^2} \right) e^{\left[A \left(\lambda - \frac{1}{\lambda} \right) \right]} \quad (4.16)$$

$$\left(\frac{\sigma_b}{\nu_e} \frac{273}{T} \right) = 3RT \left(\frac{\varepsilon_b}{\lambda_b^2} \right) e^{\left[A \left(\lambda_b - \frac{1}{\lambda_b} \right) \right]}$$

In Equation 4.16, E is the tensile modulus, ε is the strain normalized to gauge length, λ is the extension ratio (equal to $\varepsilon + 1$), ε_b is the elongation at break, ν_e is the crosslink density, and A is an adjustable constant on the order of 0.5. A plot of $\log ((\sigma_b/\nu_e)(273/T))$ versus $\log \varepsilon_b$ results in a consistent envelope of failure stress and failure strain for a variety of materials when normalized for their molecular weight between crosslinks. A graphical representation of Equation 4.16 for elastomers with different molecular weights between crosslinks as a function of elongation at break is shown in Figure 4.18.

If one assumes that the ultimate strength of the elastomer is dictated by the ultimate strength of the soft segment chains, it is expected that as the hard segment volume increases, the molecular weight between (physical) crosslinks will go down and elongation at break will decrease. This is in qualitative agreement with observations. As the hard segment traverses the phase morphology space to a co-continuous structure, the effect of increasing crosslink density on strength and elongation to break becomes more obvious as seen for example in Figures 4.15 and 4.16.

4.2.2.2 Calculating Foam Properties The properties of polyurethane foams are a convolution of the polymer physical properties with the mechanical properties of foam structure. Almost any solid can be foamed and so the concepts that qualitatively and quantitatively describe generic foam mechanical properties can be applied to polyurethane foams, at least as a starting point. In fact, it has been shown in numerous places that polyurethane foam properties are often well described by a picture of a polyurethane elastomer at lower density [59–61].

Observations of properties translating from an elastomer to a foamed elastomer are accurate, but only in a limited sense. The fact is that morphological factors that distinguish polyurethane from non-microphase separating materials (for instance polystyrene/StyrofoamTM) can have significant effects on the foaming properties. The chemical and physical processes that occur during the foam process can be quite

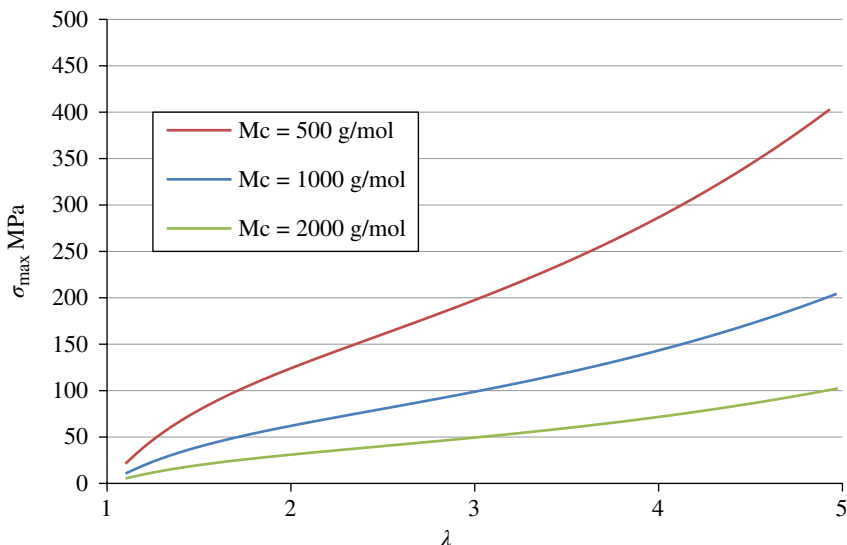


FIGURE 4.18 Graphical representation of Equation 4.16 calculating the maximum stress as a function of maximum elongation and molecular weight between crosslinks. The maximum elongation at break is arbitrarily, though reasonably, set at 400%.

different from those that occur when making a polyurethane elastomer, and they can modify the foam properties by resulting in greater or lesser phase separation, differing levels of network connectivity and molecular weight between crosslinks. All the physical concepts that create a specific polyurethane elastomer translate to the polymer morphology of the polyurethane foam, but processing conditions can result in unexpected variance. Furthermore, foam properties are highly influenced by differing choices for catalysis, and surfactancy, which can affect physical properties and cannot easily be accounted for in a predictive calculation [62].

For open cell foams, the equation relating foam's Young's and shear modulus to the modulus of unfoamed material is given by Equation 4.17. These equations are useful for a wide variety of polymers, densities, and polymer thermal properties [63].

$$\frac{E_{\text{foam}}}{E_{\text{solid}}} \sim \left(\frac{\rho_{\text{foam}}}{\rho_{\text{solid}}} \right)^2 \quad (4.17)$$

$$\frac{G_{\text{foam}}}{G_{\text{solid}}} \sim \frac{3}{8} \left(\frac{\rho_{\text{foam}}}{\rho_{\text{solid}}} \right)^2$$

Where E is the Young's modulus, G is the shear modulus and ρ the density. Measured variances from these simple relationships can be significant and can result from imperfections in foam cell struts, and the presence of closed cells or partially closed cells within the foam. Deviations from expected properties might well be expected to be sensitive to structural imperfections since the foams are usually tested in compression,

and the flexural modulus E_b , bending stress σ_b and maximum strain at the bottom surface of a bending beam ε_b are exceptionally sensitive to geometry (Eq. 4.18)

$$\begin{aligned} E_{\text{bending}} &= \frac{mL^3}{4bh^3} \\ \sigma_{\text{bend}} &= \frac{3PL}{2bh^2} \\ \varepsilon_{\text{bend}} &= \frac{6dh}{L^2} \end{aligned} \quad (4.18)$$

In Equation 4.18, L is the support span, b is the width of the beam, h is the height of the beam, m is the slope of the linear elastic portion of the load deflection curve, and P is a given point on the load deflection curve.

Closed cell foams are more complicated than open cell foams from a fundamental point of view, if only slightly more difficult from a computational perspective. Polyurethane foams are made from an initial liquid state. As the chemical and physical processes proceed to form a foam, material will be drawn from the expanding cell bubble into the edges. In open cell foam, cells matriculate as closed cells up until the thinning cell face membrane ruptures and open cells percolate a continuous open channel from one end of the foam to the other. In the case of closed cell foams, the internal gas pressure that builds within the individual cell bubbles is insufficient to break the thinning cell face membrane prior to the system vitrifying [64]. In this case, a substantial amount of the foam tensile properties will be due to the foamed material contained within the cell faces.

An additional contribution to cell tensile properties will be made by the gas that is trapped within the closed cells. If the sample is compressed by given strain ε , the volume of the foam decreases given by Equation 4.19 where ν is Poisson's ratio.

$$\frac{V}{V_o} = 1 - \varepsilon(1 - 2\nu) \quad (4.19)$$

However, the gas only occupies the space not occupied by the foam bubble edges and faces, so that the gas volume decreases by

$$\frac{V_g}{V_g^o} = \frac{1 - \varepsilon(1 - 2\nu) - (\rho / \rho_s)}{1 - (\rho / \rho_s)} \quad (4.20)$$

where ρ/ρ_s is the ratio of the foam density to the solid density. The change of the cell internal gas pressure upon compression is given by Boyle's law.

$$pV_g = p_o V_g^o \quad (4.21)$$

The pressure resisting compression and contributing to the foam stiffness is the difference between the calculated p and the internal gas pressure under no strain (p').

Thus the contribution of the gas trapped within closed cells to the foam modulus is given by Equation 4.22.

$$E_g = \frac{dp'}{dp} = \frac{P_{o(1-2\nu)}}{(1-(\rho/\rho_s))} \quad (4.22)$$

Thus, the modulus of the closed cell foam can be calculated from a simple additivity assumption as equal to the sum of moduli from the cell edges, cell faces, and internal gas pressure (Eq. 4.23) [63].

$$\frac{E_{ccf}}{E_s} = \varphi^2 \left(\frac{\rho}{\rho_s} \right)^2 + (1-\varphi) \left(\frac{\rho}{\rho_s} \right)^2 + \frac{P_{o(1-2\nu)}}{(1-(\rho/\rho_s))} \quad (4.23)$$

$$\frac{G}{E_s} = \frac{3}{8} \left[\varphi^2 \left(\frac{\rho}{\rho_s} \right)^2 + (1-\varphi) \left(\frac{\rho}{\rho_s} \right)^2 \right]$$

Where φ is the fraction of solid in the bubble edges and $1-\varphi$ is the fraction in the cell faces. There is no shear modulus contribution from the cell internal gas pressure so it does not appear in that equation. Figure 4.19 compares the modulus ratio of the foam

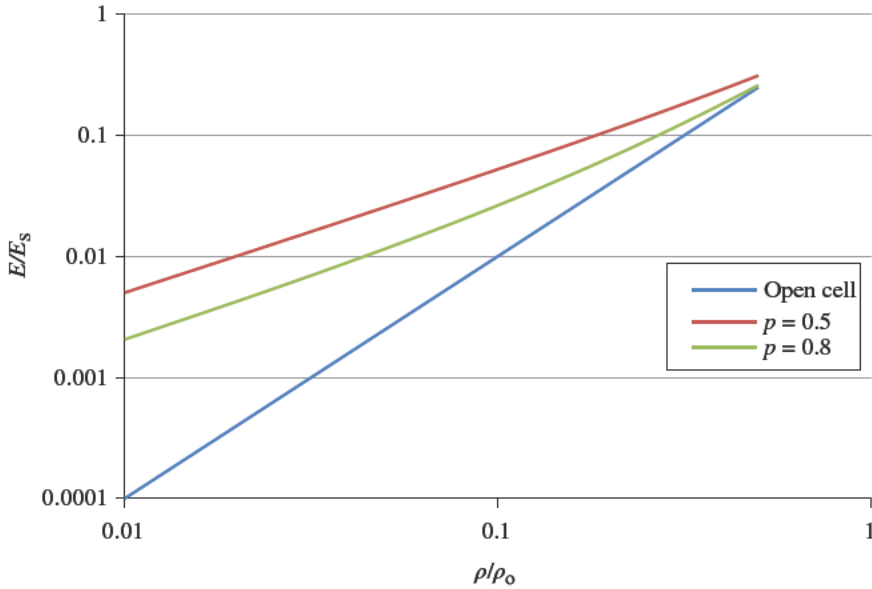


FIGURE 4.19 Graphical representations of Equations 4.17 and 4.23 showing the modulus ratio of foam to its solid polymer as a function of density and the fraction of polymer in the cell edges (φ).

to the unfoamed polymer as a function of the ratio of the foam to the solid density using Equations 4.17 and 4.23. For reference, a rigid (closed cell) polyurethane foam has been reported to have a φ value of 0.8 [65].

4.2.3 The Polyurethane Glass Transition Temperature

Figure 4.13 defines the tensile properties of polyurethanes in relation to the phase separated hard and soft segment glass transition temperatures. The glass transition temperature is certainly one of the more difficult physical parameters to treat from a theoretical perspective due to its “nonunique” nature [66]. This nonunique distinction is manifested in the value being a function of how it is measured (such as the rate of measurement), whether the transition is approached from low or high temperatures, and also by the instrumental technique. It is also problematic that the glass transition is not well defined by a single temperature but by a temperature region, with a finite and sometimes very substantial breadth (e.g., Fig. 5.24). In such cases, the glass transition temperature will be treated as a specific point in an instrumental response curve, but this is often more by convention than actual utility [67].

Theoretical approaches to the polymer glass transition temperature typically treat measured T_g values as kinetic manifestations of underlying thermodynamic interactions between polymer segments, end groups, and additives. The specifics of these interactions can vary widely. Furthermore, disagreement on the thermodynamic definition of glass transition temperature relative to discontinuities in thermodynamic quantities further complicates first principle theoretical treatment. Nevertheless there are numerous equations that are used in practice and in the scientific literature to estimate the glass transition temperature of polyurethanes. Many of these equations are semi-empirical, requiring input of measured data obtained from pure materials to make calculations based on interpolation. Others use measured reference values combined with fitting parameters that are defined in elaboration of fundamental principles. The choice of which equation a practitioner uses will depend on the individual's preferences and access to data that might be required for refined prediction of values. Another method has utilized group additivity principles which can result in relatively good predictions if enough group factors are incorporated. Specific methods and values using group additivity principles have been presented [68].

One of the most common equations used for predicting the glass transition temperature of binary systems of which polyurethanes might be considered is the Fox equation (4.24) [69]. The exceptionally simple form and the sole need to obtain the glass transition temperatures of the pure components (which can normally be measured or even estimated with good precision) make it widely used. The simplicity of the equation is an expression of the numerous underlying assumptions. These assumptions are that the pure material glass transition temperatures are constant with blend composition; that the contributions of the polymer components are additive (a small molecule plasticizer or a polymer blended with a polymer have equivalent

effects), symmetrical on their influence on the glass transition temperature; that the two polymers are miscible and amorphous; and that the heat capacity changes at the phase transition are the same for the two materials.

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \quad (4.24)$$

In Equation 4.24, T_g represents the glass transition of the miscible blend while w_i represents the weight fractions of the respective polymer components and T_{gi} the glass transition of the pure polymer component. The graphical representation of Equation 4.24 is given in Figure 4.20. It shows the weak T_g depression that results from mixing two materials due to the slight increase in free volume and entropy in the absence of specific interactions. This is visualized by comparison to the graphed function in which the blend T_g is represented by a function in which the T_g s are simply added in a mass weighted linear combination.

The Fox equation is in fact a special case of the Gordon-Taylor equation (Eq. 4.25) [70]. This equation is very widely and successfully used containing the assumptions of the Fox equation but introduces a parameter (k). k depends on the specific volume of the components (V) and the thermal expansion coefficients α . In practice, k is usually treated as a fitting parameter but should be on the order of 1. Practically this parameter allows for asymmetry between the blend component contributions to the blend T_g . This would allow for a physical situation in which the contribution of blend component 1 to the blend glass transition temperature is weighted disproportionately

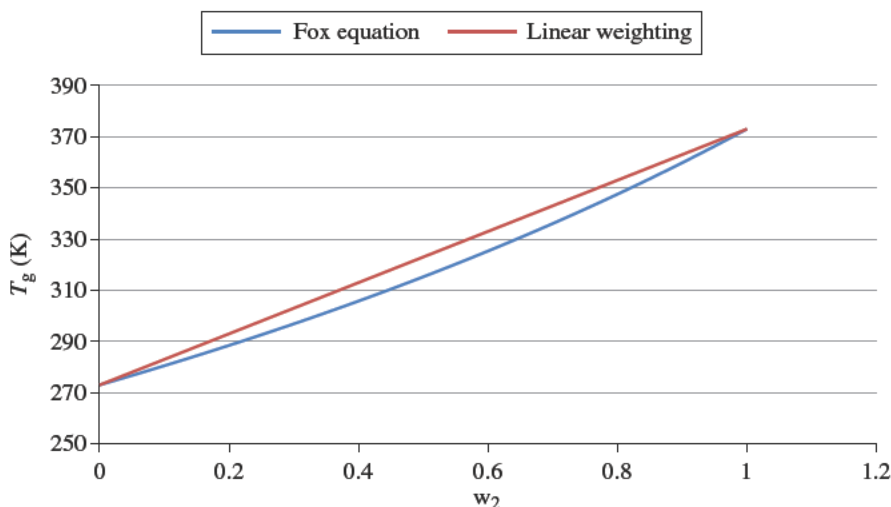


FIGURE 4.20 Graphical representation of the Fox equation (4.24) relative to a simple mass weighted linear combination of pure material T_g s. For illustration, T_{g1} was chosen to be 273 K and T_{g2} was chosen to be 373 K—relevant to many polyurethane systems.

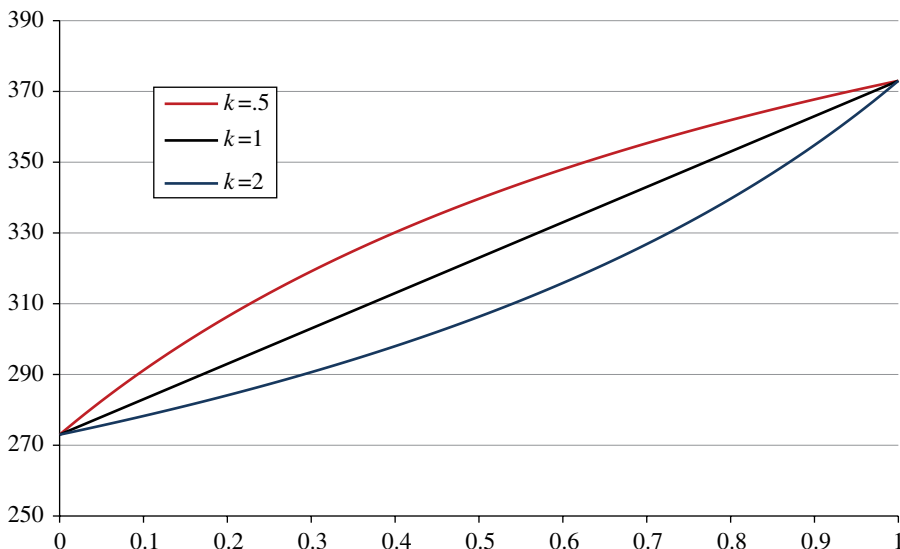


FIGURE 4.21 Graphical representation of the Gordon-Taylor equation for varying values of k yielding either positive or negative deviations from a mass weighted linear combination of pure material glass transition temperatures.

to that of component 2, resulting in a stronger deviation (see Fig. 4.21) than predicted by the Fox equation.

$$T_g = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2} \quad (4.25)$$

$$k = \frac{(\rho_1 T_{g1})}{(\rho_2 T_{g2})} \quad (\text{The Simha – Boyer rule})$$

The Fox equation can be derived from the Gordon-Taylor expression as a limiting case of the Simha-Boyer rule for k in Equation 4.25 where specific volumes of the components are treated as identical, that is, $k \sim T_{g1}/T_{g2}$ [71].

A special case of the Gordon-Taylor equation offered by Ginzburg and Sonnenschein [38] was developed specifically for polyurethanes reflecting microstructural details as described by Figures 4.6 and 4.17. Equation 4.26 specifies the T_g for the soft segment depending on the amount of dissolved hard segment in the soft segment (w_H). The dissolved hard segment is a function of the microphase structure defined by Figure 4.6 and quantitatively Equation 4.3 by variable χ_o^N .

$$T_g = \frac{w_H T_{gH} + k(1 - w_H) T_{gs}}{w_{iH} + k(1 - w_H)} \quad (4.26)$$

$$w_H = \text{HSWF for } f_{(DS)} > \text{HSWF}$$

$$= \frac{f_{DS}}{1 - [\text{HSWF} - f_{DS}]} \text{ for } f_{(DS)} < \text{HSWF}$$

In this variation of Gordon-Taylor formalism, if the hard segment weight fraction is below the order disorder transition (the D-S isomorph of Fig. 4.6) the fraction hard segment in the soft phase is the total hard segment mass in the polymer. However, if the polymer has a phase-separated microstructure, the amount of hard segment in the soft phase reflects the total hard segment minus the amount of hard segment that has precipitated into a separate phase.

An occurrence sometimes encountered in polymer blends is that two polymers interact through a specific and relatively strong interaction. Such an interaction would be, for instance, strong hydrogen bonding between blend components. In this instance, significant deviations from the previous equations may be observed. For this case, the Kwei equation 4.27 has been utilized for systems exhibiting both negative and positive deviations from the linear combination profile (Fig. 4.22) and “S” shaped profiles [72].

$$T_g = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2} + q w_1 w_2 \quad (4.27)$$

The functional versatility of the equation results from the quadratic function in the second half of the equation. While k and q are usually treated as fitting parameters, there has been significant investment in creating a fundamental justification and

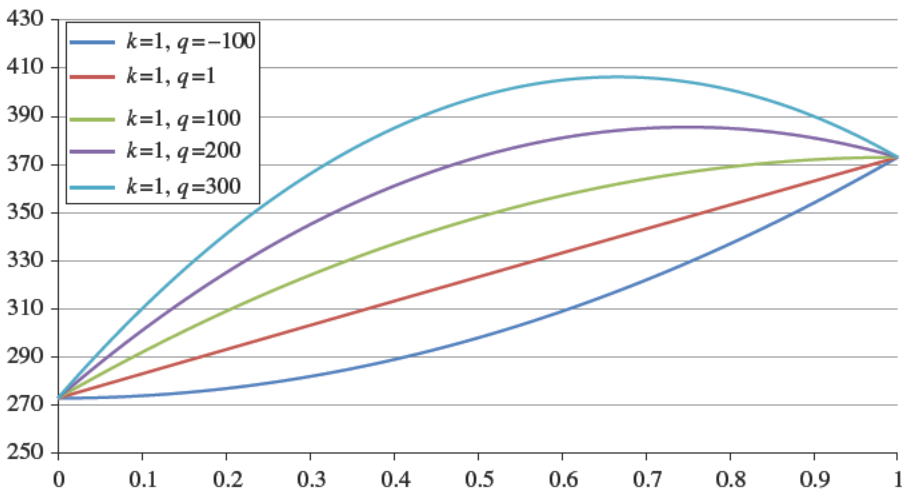


FIGURE 4.22 Graphical representation of the Kwei equation keeping k at or near one (as in the Gordon-Taylor formalism) and varying q to demonstrate its effect on the functional form.

elaboration for the q variable as it relates to the intermolecular interactions responsible for the observed T_g behavior [73, 74].

Another equation employed in the case of significant deviations from a simple weighted linear combination of glass transition temperatures was offered by Lu and Weiss [75]. It is also a modification of the Gordon-Taylor equation (as is the Kwei equation) and incorporates a quadratic dependence as the Kwei equation does. However, the q value is elaborated in terms of the Flory χ value which can be obtained by a best fit routine (Eq. 4.28). In Equation 4.28, b is the ratio of amorphous densities of polymer 2 and polymer 1, ΔC_{p1} is the change in specific heat of polymer 1 at T_{g1} , and the other variables are as previously defined for the Gordon-Taylor equation. In cases where the blend polymer interactions are quite strong, this equation has shown utility and resulted in reasonable values of χ . In the case of weak or moderate interactions, the Gordon-Taylor equation has provided equally predictive results to the Lu and Weiss equation [76].

$$T_g = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2} - \frac{\chi R (T_{g2} - T_{g1}) b w_1 w_2}{\Delta C_{p1} (w_1 + k w_2) (w_1 + b w_2)^2} \quad (4.28)$$

While all of these equations have been applied to polyurethanes, there are quite a few other approaches that have been tried or could be applied [63, 77–81].

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5

ANALYTICAL CHARACTERIZATION OF POLYURETHANES

Advances in instrumentation coupled with computerization and information technology have greatly advanced our understanding of urethane chemistry and polyurethane materials. This increased knowledge base has resulted in greater predictability in polyurethane use and increased proliferation of polyurethane materials across the spectrum of applications. Modern methods of analysis have permitted nearly every kind of time- and frequency-resolved analysis. Morphology can be characterized down to angstrom levels allowing confident distinction between subtle differences in phase structure and mixing between materials. Prediction of properties, making of materials, and proper application of polyurethanes now require that a practitioner be familiar with the operation of numerous analytical instruments. Even more crucial is the understanding of the data produced by analyses and the ability to perform root cause analyses of material or application failure based on that data. This chapter will provide an introduction to selected experimental techniques and more in-depth discussion of the connection between data and its use. Although information is almost always useful, gathering information can be wasteful if the measurements do not apply directly to the problems to be solved. This chapter will also provide guidance on the most efficient methods of determining the root cause of material or application failure.

Before a material can be tested or applied, it must be made, and the incorrect making of a polyurethane is one of the most common causes for disappointing performance. The properties of a polyurethane are critically dependent on the proper ratio of reactants being joined, and determining the correct ratios requires accurate measurement of reactant functionalities. As discussed in Chapters 2 and 3, there are numerous unintended

side reactions that can occur in the preparation of polyols and isocyanates that can significantly affect the amount of hydroxyl or isocyanate functionality in a given weight of material. Incorrect measurement of reactant functionalities can have many negative effects on final physical properties, primarily by resulting in reduced final polymer molecular weight or an incomplete network structure.

It is nearly impossible to employ perfect stoichiometric ratios when making a polyurethane; however, it is possible to be close enough that a high final molecular weight polymer network is formed that molecular weight is not the limiting factor driving polyurethane performance. The first and most critical initial step to making high-performance polyurethane materials is accurate measurement of the hydroxyl and isocyanate functionality per unit mass. ASTM is an organization that provides industry-defined, accepted, and explicit methods for performing these analyses. They provide a basis for confidence that all manufacturers of polyurethane building blocks are producing materials that can be used to make a desired material using normal laboratory techniques. The ASTM also provides guidance on alternative ways of obtaining the same piece of information using different analyses that can substitute if a particular technique is not accessible or if independent methods of measurement of the same quantity are desired. Furthermore, ASTM methods provide a gauge of measurement reliability and thus a means of determining if a measurement is being made with the proper level of precision to meet an industrial level of expectation.

5.1 ANALYSIS OF REAGENTS FOR MAKING POLYURETHANES

5.1.1 Analysis of Polyols

There are several analyses that accompany virtually every batch of industrially produced polyol. These are indicated in Table 5.1 along with the relevant ASTM method developed to measure the property.

TABLE 5.1 Conventional polyol specifications and ASTM procedures for measurement

Property	ASTM method
Hydroxyl number	D4274 measurement by derivatization and titration
Hydroxyl number	D6342 measurement by near-infrared spectroscopy
Viscosity	D4878 measurement by Brookfield viscometry
Controlled polymerization rate (CPR)	D6437 measures alkalinity remaining from glycol polymerization that can affect subsequent isocyanate polymerization
Unsaturation	D4671 titration method uses mercuric acetate in a methanol solution
Cloud point	D2024 standard test method for nonionic surfactants
Water content	D4672—Karl Fischer colometric titration technique for alcohols or E203 general Karl Fischer titration method

The application of these standard techniques will invariably result in a number whose precision can be well characterized by replicate samples. However, the ability to get optimal polymerization results will depend on the accuracy of the result. There is no a priori means of knowing if the analytical result a practitioner is handed is useful. The result of a poor analysis is a polyurethane with poor properties, and it will be ambiguous if the problem is a result of analysis or polymer design [1]. The practitioner should never simply accept the result of a single experiment and should always be suspicious of the polyol analysis, particularly the hydroxyl value. It may be necessary to bracket the polymerization, assuming the measurement of the property is wrong by as much as 10%. This may require a new polymerization attempt at the analyzed value and additional attempts at a ratio 10% greater and 10% less than the measured value. Improved polymer properties in either direction may require additional empirical iteration. Table 5.2 lists the polyol quality tests of Table 5.1 and a relative evaluation of the reliability of the test based on statistical analysis within labs and between labs (this information is usually provided within the standard). The discrepancy is often a result of systematic operator errors, differences in execution of the ASTM tests (i.e., catalysts, solvents, etc.), and the use of autotitration [1] versus manual titration techniques. The author has observed that unless an autotitrator is employed by a very experienced and methodical technician, the manual titration is more likely to provide a reproducible result.

Each of the tests in Table 5.1 can be potentially important; however, the hydroxyl number and the CPR value are the variables that can greatly affect the final result of the polyol use.

5.1.1.1 Hydroxyl Number Measurement of hydroxyl number is usually obtained by the derivatization and titration technique. The general procedure is to carry out an esterification reaction of the alcohol with an anhydride, usually phthalic or acetic (Fig. 5.1) [2]. The need to react all of the alcohol groups necessitates the use of an excess of anhydride, and a strong base catalyst (i.e., standard 0.5 N NaOH_{aq} or imidazole). The reaction is often run in pyridine solvent and carried out at elevated temperatures (ca. 100 °C) for up to 2 h. A blank (i.e., no polyol) is run side by side, and the amount of acid is subsequently titrated using an indicator such as

TABLE 5.2 Critical evaluation of the ASTM method derived property value in Table 5.1. manufacturer numbers on well-established products are usually reliable. New materials made by new processes may be far less so

Property	Reliability
Hydroxyl number derivatization method	Below average
Hydroxyl number near-IR spectroscopy method	Above average
Viscosity	Above average
Controlled polymerization rate) (CPR)	Average
Unsaturation	Average
Cloud point	Average
Water content	Below average

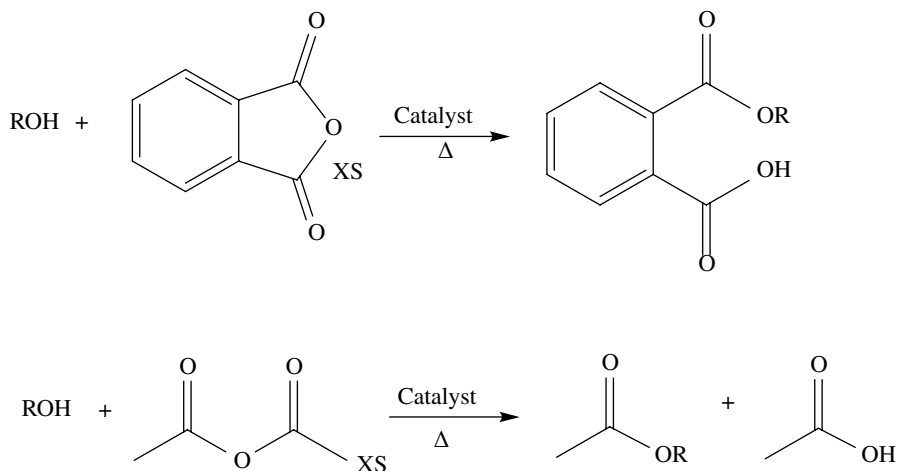


FIGURE 5.1 Anhydride derivatization of polyols prior to titration of acid end groups for determination of OH number.

phenolphthalein for colorimetric endpoint determination. The procedure is sufficiently exacting that operator experience and exactitude are a must to obtain usable results.

The hydroxyl number in units of milligrams KOH/gram of sample is calculated from Equation 5.1:

$$[(A - B)N \times 56.1] / W \quad (5.1)$$

where A is the milliliters of NaOH required for titration of the blank, B is the milliliters of NaOH required for titration of the sample, N is the normality of the NaOH solution, 56.1 is the equivalent weight (grams/equivalent) of KOH, and W is the weight of the sample used. The weight percentage of OH in the sample is given by Equation 5.2 where 17 is the equivalent weight of the OH functionality [3]:

$$\frac{[(A - B)N \times 17 \times 100]}{\text{mg sample}} \quad (5.2)$$

The application of an inaccurate hydroxyl number will result in materials with low polymer molecular weight and poor network formation resulting at the minimum in degraded break elongations and, at worst, a viscous mess.

When performed correctly, the precision of the measurement at the 95% confidence level is about 1% and is of similar reliability. It can be used for almost all polyols (polyether, polyester, polycarbonate, and amine initiated). Many common additives such as most fire retardants, antioxidants, and catalysts do not interfere with the precision or accuracy of the measurement. Excessive water (capable of hydrolyzing

the anhydride and biasing the OH number to lower values) and primary or secondary amines, also able to react with anhydrides, do have the potential to interfere with the titrimetric evaluation of polyols. Lastly, if the sample contains intrinsic acidity or alkalinity prior to derivatization, the results must be corrected. The ASTM standard provides an explicit method for the correction of a sample having intrinsic acidity (biasing the result toward lower hydroxyl numbers) or alkalinity (biasing the result toward higher hydroxyl numbers) that can interfere with the titration of derivatized acid end groups.

An alternative means of measuring the percentage hydroxyl in a sample is by infrared (IR) spectroscopy. ASTM specifies the method and use of commercial near-IR instruments for the measurement. This technique is dependent on calibration curves of characteristic OH absorbance in the 5000–9000 cm^{-1} region. Absorption in this region is relatively weak, and there are relatively fewer resonances [4, 5]. While mid-IR spectra can also be used [6, 7], the weak absorption of the near IR is an advantage in this case since it allows thicker samples for transmission. As a secondary method, its reliability depends on the calibration curve. However, if a reliable calibration curve can be obtained and the instrumental application can be standardized, near-IR techniques can result in more reliable determination of hydroxyl values than titration techniques since human systematic error is minimized [8]. The greater potential reliability of the near-IR technique has been documented in industrial round-robin testing [9].

Modern IR techniques, especially attenuated total reflectance (ATR) spectroscopy, open up the potential for very rapid and convenient measurement of hydroxyl number and change of hydroxyl number during a reaction. The ATR technique eliminates problems associated with high absorbance causing instrumental response to no longer function in the detector's linear range. The experiment requires that the sample be dry and not have competing resonances due to N–H bonds. When these conditions are fulfilled, the O–H stretch resonance (between 3100 and 3600) can be isolated with baseline resolution (Fig. 5.2) from other absorption peaks, integrated (usually with instrument supplied software) and compared to an appropriate calibration curve constructed from structurally related polyols (Fig. 5.3).

5.1.1.2 CPR Another standard polyol analysis is the CPR measurement providing an indication of the trace basicity left in the polyol following production. This is a particularly important variable for individuals involved in preparation of prepolymers (isocyanate-terminated polyols; see Section 2.1.6). The importance of CPR reflects the fact that the vast majority of polyols are produced using base catalysis. Although modern manufacturing practice has numerous means of nearly eliminating the free base left after production, there is normally a trace of basic activity left in the polyol sample being used for polyurethane or prepolymer preparation. This leftover base activity can have negative influences on prepolymer shelf stability due to the ability of base components to catalyze isocyanate–isocyanate reactions. The actual basic components present are not identified but are simply the total weak acid salts left in the sample. Since the amount of base active

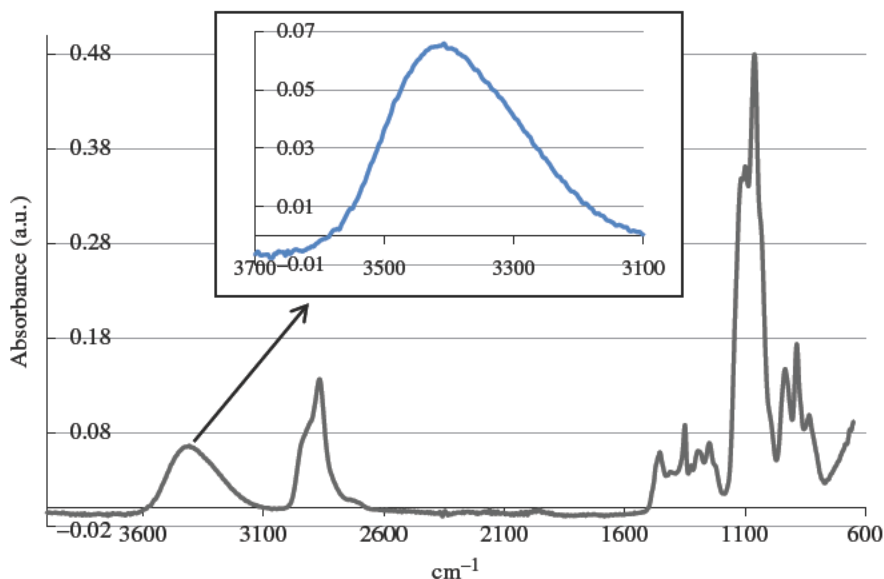


FIGURE 5.2 Attenuated total reflectance FTIR spectroscopy of polyethylene glycol of molecular weight 200. The inset is a magnification of the hydrogen-bonded OH absorbance, which can be area integrated as part of a calibration curve.

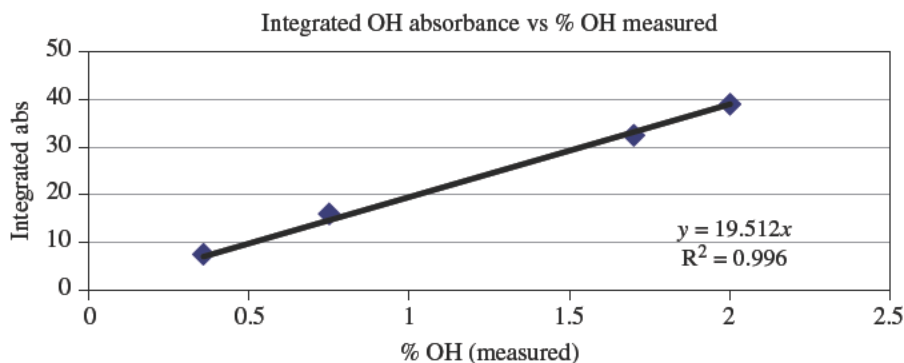


FIGURE 5.3 Example calibration curve generated for FTIR determination of OH content of polyols.

elements left after manufacture and processing is usually small, a large sample of polyol must be employed for the test. The reported number is in units of milliequivalents of KOH/30kg of sample or often 10 times that number. The typical CPR values are from about 0.1 to 1 [or 1–10]. The net CPR reflects that when mixed with an isocyanate, net acidity from the manufacture of isocyanate (in the form of HCl; see Chapter 2) can in part counterbalance the basicity of the polyol. Thus, the net CPR is given by Equation 5.3:

$$\text{Net CPR} = \text{CPR}_{\text{polyol}} + \text{AHC}_{\text{isocyanate}} \quad (5.3)$$

where $\text{AHC}_{\text{isocyanate}}$ is the active hydrolyzable chloride in the isocyanate. A high net CPR will result in poor prepolymer shelf life and poor polyurethane formation due to uncontrolled catalysis. The CPR test itself is a titration to an indicated endpoint or readout of a potentiometric electrode. The calculation is based on Equation 5.4:

$$\text{CPR} = (V_{\text{sample}} - V_{\text{blank}}) \times N \times 30,000 / W \quad (5.4)$$

where V_{sample} is the volume of titrant (0.01 N HCl) to the last endpoint or potentiometric break, V_{blank} is the volume of titrant to the last break in blank titration, N is the normality of HCl, 30,000 is the conversion factor for 30 kg, and W is the weight of the sample. As indicated in Table 5.2, the precision of this test ($\pm 20\%$) is average at best based on round-robin industry testing and depending strongly on the skill of the practitioner. Thus, CPR measurement reliability should always be suspect if prepolymer shelf life stability is an issue.

5.1.2 Analysis of Isocyanates

Isocyanate functionality and the quality of the isocyanate used for polyurethane polymerization are as critical to the final material result as the polyols. However, the characterization of isocyanates is in some ways easier since, with the exception of polymeric MDI (pMDI), they are monomeric and can be distilled to a pure state or possess an isomeric distribution that is relatively easy to characterize using modern analytical techniques. Another distinction with polyols, isocyanates are somewhat easier to titrate than alcohol groups since their reaction with amines is diffusion limited. Just as with polyols, ASTM provides several explicit standard methods for characterizing an isocyanate sample, and given the advantages of characterizing the isocyanate monomers and functionality, the tests exhibit superior precision and reliability to those for polyols. However, the reactivity of isocyanates does not permit the practitioner to trust the functionality per unit mass. Given the number of isocyanate–isocyanate (see Chapter 3) reactions and the facile reaction of isocyanate with opportunistic water, the quality of an isocyanate should always be regarded with suspicion if a reaction is not proceeding as anticipated.

There are a number of ASTM techniques applicable to isocyanates. Many of them relate to safety and air monitoring for isocyanates. Table 5.3 is a partial list of ASTM methods related to the use of polyisocyanates, the values of which might be included on a certificate of analysis from a manufacturer and relate to the reliability in use.

There are several other standards available associated with, for instance, measurement of viscosity, color, and density, but these are related more to manufacturing control than reliability in use. As alluded to, the reliability of these tests can be expected to be good as enumerated in Table 5.4.

Since the tests for isocyanate quality are expected to be relatively reliable, there is a reasonable expectation that the values attending a particular product were trustworthy at the time they were made. Problems in polyurethane properties that

TABLE 5.3 Conventional isocyanate specifications and ASTM procedures for measurement

Property	ASTM method
Percentage hydrolyzable chloride	D5523 potentiometric method following reaction of sample with isopropanol to form HCl
Percent MDI monomer in pMDI and monomer isomer distribution	D7252 method of HPLC separation resulting in baseline resolution of species and well-determined elution times
Determination of isocyanate content per unit mass	D5155 titration of isocyanate with a secondary amine (dibutylamine) followed by titration of excess amine
Standard specification for TDI	D1786 methods and expectations for TDI based on purity, color, total chlorine, hydrolyzable chlorine, isomer distribution
Isomer content of TDI	D4660 employs IR spectroscopy using standard materials and internal standard for quantification

TABLE 5.4 Critical evaluation of the ASTM method derived property value in Table 5.1. Manufacturer numbers on well-established products are usually reliable. New materials made by new processes may be far less so

Property	Reliability
Percentage hydrolyzable chloride	Unknown but expected to be average
Percent MDI monomer in pMDI and monomer isomer distribution	Very good
Determination of isocyanate content per unit mass	Very good
Standard specification for TDI	NA
Isomer content of TDI	Very good

may result from poor isocyanate quality are generally a reflection of poor storage conditions or unoptimized handling during the polymerization. It is often the case that a slight excess of isocyanate is added to the polymerization to account for loss of unit mass content of isocyanate. This addition can be from about a 1–5% excess isocyanate equivalence. Experience is the best guide here.

In many applications using pMDI, it is found that the performance of a particular manufacturer's product will consistently vary from that of another. While this could be a reflection of systematic handling differences, it is often the case that the composition of the pMDI is sufficiently different that the resulting polyurethane performance is significantly affected. Compositional differences can reflect numerous manufacturing process variables as well the amount of 4,4'-MDI monomer that is distilled from the crude product. Thus, the practitioner should understand that when using pMDI, it may be necessary to analyze according to ASTM 7252 for composition to understand the results and perhaps develop a more useful patent strategy when involved in innovation and patent application filing.

5.1.2.1 Analysis of pMDI Composition ASTM 7252 is an explicit method to determine the composition of pMDI using high-performance liquid chromatography (HPLC). The method depends on the use of acetanilide as an internal standard and employs calibration curves based on pure standard samples obtained from well-known chemical suppliers. The precision of this method based on round-robin testing is about 1%. Example chromatograms are found in the standard. The percentage of a given isomer based on the chromatographic data using an internal standard based on integrated peak areas is given by Equation 5.5:

$$\text{Isomer}_i (\%) = \left[\frac{A_i^{\text{sample}} A_{\text{IS}}^{\text{std}} W_i^{\text{std}} \times 100}{A_i^{\text{std}} A_{\text{IS}}^{\text{sample}} \times W_{\text{sample}}} \right] \quad (5.5)$$

where A_i^{sample} is the area of the I isomer peak in the chromatogram, $A_{\text{IS}}^{\text{std}}$ is the area of the internal standard in the standard chromatogram, A_i^{std} is the area of the I isomer in the standard chromatogram, $A_{\text{IS}}^{\text{sample}}$ is the area of the internal standard peak in the sample chromatogram, W_i^{std} is the weight of the I isomer in the standard solution, and W_{sample} is the weight of the unknown sample.

Many laboratories use gas chromatography (GC) for this analysis when HPLC is not convenient, employing a diphenylmethane internal standard, but this is not suggested in the ASTM method. GC analysis is considered to be reliable to a precision less than 1% standard deviation for these measurements [11]. Size-exclusion chromatography has also been demonstrated and found to be reasonably reliable with a precision of about 1% becoming slightly less reliable for quantitative determination of the higher-molecular-weight oligomers (pentamers and higher) [12].

5.2 INSTRUMENTAL ANALYSIS OF POLYURETHANES

Modern technology has developed the means to acquire data at relevant length scales such that many aspects of polyurethane morphology and function can be readily understood. Many techniques offer corroborating as well as extending information. For instance, it is often the case that characteristic phase separation lengths visibly discernable by atomic force microscopy (AFM) can be validated by small-angle X-ray scattering (SAXS). The SAXS data in addition can be further interpreted for information about the boundary between the hard and soft phases. An elastomer that exhibits slow elastic response by touch can have its room temperature glass transition temperature corroborated and quantified by dynamic mechanical analysis (DMA). Modern instrumental techniques have become so disseminated and accessible to experimentalists that it is now expected that data obtained by a single technique leaves too many questions unanswered to be compelling. Experimentalists now routinely apply numerous techniques to a single material [13–18]. The use of these techniques, apart and in unison, has allowed scientists unprecedented understanding of polyurethane morphology and enabled theoretical analyses that further deepen our understanding and predictive capabilities.

5.2.1 Microscopy

Microscopy of polyurethanes is of great interest because its evaluation can span length scales from millimeters to nanometers. Since important polyurethane structures express themselves across these lengths, the information obtained at one scale may often be corroborated at another length scale [19]. For instance, a polyurethane specimen may be prepared and be either transparent or opaque. The cause of this optical distinction can usually be ascribed to phase characteristics of the urethane blocks [20], composite additives that when of sufficient size will scatter visible light or artifactual air bubbles. The samples can subsequently be observed by scanning electron microscopy (SEM) for the micron to 100s of micron scale, which may confirm the presence of phase separated copolymer particles (see Chapter 2), soft segment crystals, composite additives, or gas bubbles generated by the inadvertent reaction of isocyanate and water to form CO_2 . Or the SEM may reveal no feature of sufficient contrast applied to an optically transparent specimen. Transmission electron microscopy (TEM) (10–1000s nm) may be employed with specialized stains to increase contrast between phases and to reveal phase separated hard segments that are spherulitic or lamellar. Lastly, AFM (1–100s nm) may be applied to the sample to reveal phase separated spherical structures developed as a result of a nucleation and growth (opaque), the lacy structures developed from spinodal phase decomposition, or the stunted phase structures associated with incomplete phase separation resulting from polymer vitrification [21].

5.2.1.1 Optical Microscopy Although one of the most readily accessible tools in modern analysis, optical microscopy only finds occasional use in modern polyurethane research. Modern techniques of optical microscopy are well covered in various books and reviews devoted to the subject [22–24]. Use of optical microscopy for the study of polyurethanes often exploits the ability to polarize the light from the light source and so illuminate crystal structures that may evolve as a result of soft segment crystallization or formation of mesophase (liquid crystalline) structures [25, 26]. The use of a hot stage is well applied in this work since it allows the slow melting/recrystallization of a material to be observed in real time [27]. Optical techniques allow for a descriptive evaluation of the phase structure (i.e., spherulitic, lamellar, etc.) often accompanied by quantitative thermodynamic measurements obtainable by differential scanning calorimetry [28]. Measurements such as these can be compelling especially when applied to highly systematic structural studies that can track the size of crystallites as a function of some molecular parameter [29, 30].

Classical optical microscopy can find uses as well for gross descriptions of polymer wear, aging, and forensic analysis. Other uses of optical microscopy can be frustrated by the mismatch of relevant scales of interest, poor contrast between phases, interference by light scattering off of a top surface, poor transmission of light through a polymer film, and light scattering off of the myriad surfaces offered by a foam specimen. Modern techniques in optical microscopy, such as optical phase contrast imaging, can provide more information than other optical techniques by increasing contrast between phases (Fig. 5.4) [31]; however, other techniques such as TEM and AFM can provide a higher degree of resolution and are more widely used.

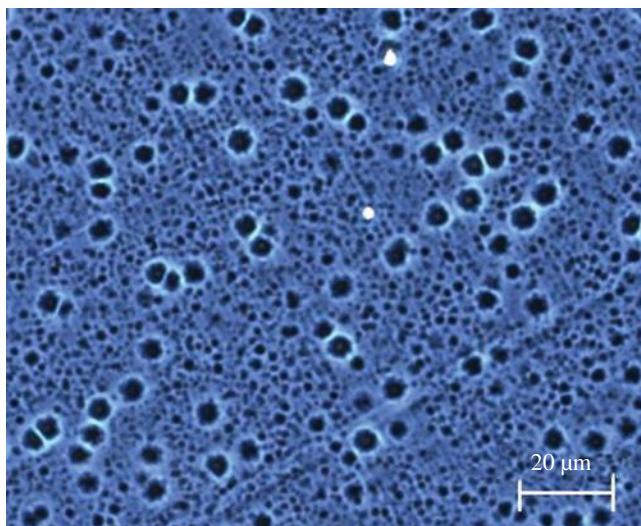


FIGURE 5.4 Phase contrast optical microscopy of a cast polyurethane elastomer—dark areas are hard segment. See Figure 5.6 for comparative image quality and information content versus TEM. Image courtesy of Robert Cieslinski and Justin Virgili. (*See insert for color representation of the figure.*)

5.2.1.2 SEM SEM is a broad field of analysis that has improved dramatically over the years [32]. Resolution of electron microscopy rivals that of TEM and AFM. An electron beam from a heated filament is focused and scans the surface of a sample in a raster pattern. The electrons interact with the materials of the surface and are absorbed, scattered, or reflected. Reflected or secondary electrons generated from the specimen as a result of the electron beam collision, or electromagnetic radiation, can be subsequently detected depending on the microscope hardware. A representation of the surface is generated after electron surface collisions are detected and correlated with an x , y coordinate on a display. The resulting images can have tremendous verisimilitude and produce three-dimensional depth of high fidelity.

SEM is very commonly used in polyurethane research, but because the signal is primarily a representation of surface features, there are limitations. SEM is often used to image gross images of polyurethane structures such as foam cell structure that can be more difficult with optical techniques due to incident light scattering. Figure 5.5 shows an SEM of an open-cell foam. Notice that the magnification is not particularly high, but the same picture by optical microscopy would typically not contain the observed level of detail. SEM is also commonly utilized to visualize polyurethane 2-phase composites such as fiber- and mineral-reinforced structures and their interfacial features. Such an image of a urethane composite is shown in Figure 5.5b showing high levels of adhesion of urethane to the embedded glass fiber.

Hard segment and soft segment do not scatter electrons with sufficient distinction to be separately observable since PU samples are normally coated with a conductive layer such as gold to conduct electrons away from the surface and reduce deresolution

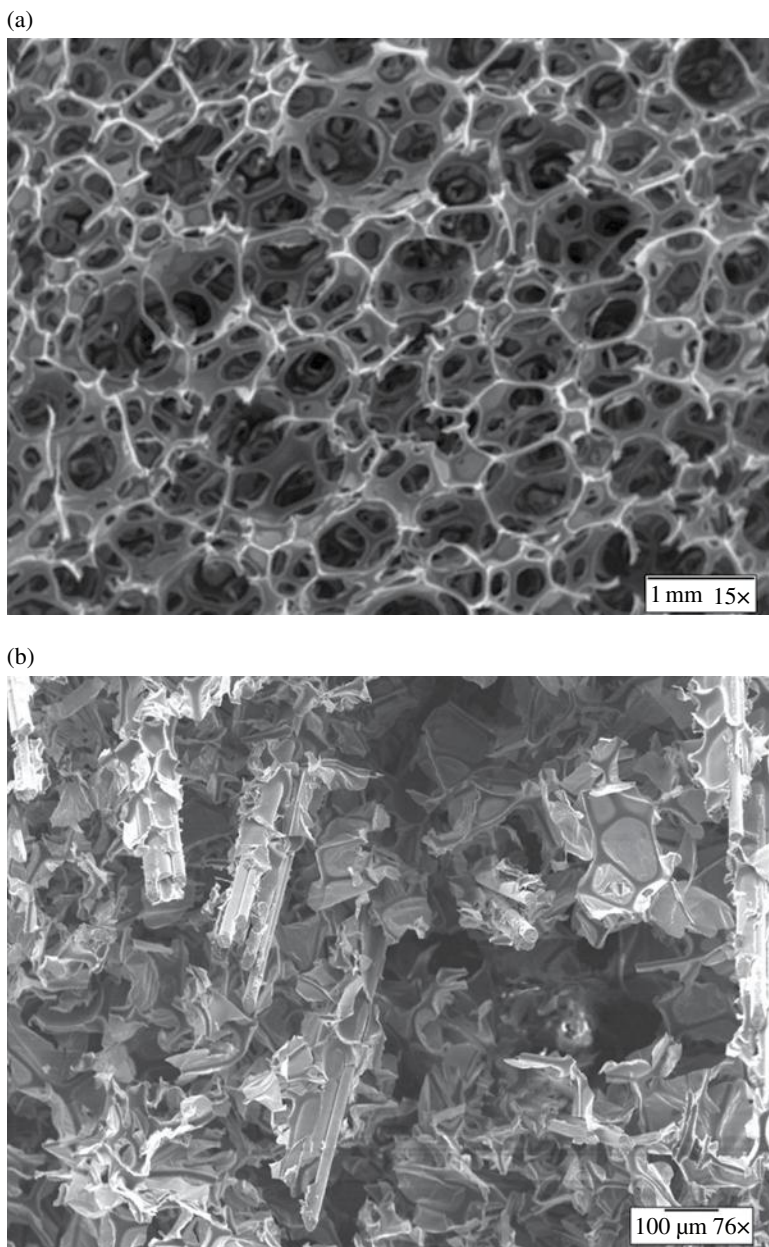


FIGURE 5.5 Illustrative scanning electron micrographs of (a) open-cell polyurethane foam and (b) glass-filled polyurethane insulation foam composite.

of the image caused by electron scattering from a negatively charged insulating PU sample. Gross changes in fracture surfaces at different hard segment contents have been rationalized as demonstrating the effect of hard segment, but do not reveal the hard segment structure observed by other techniques.

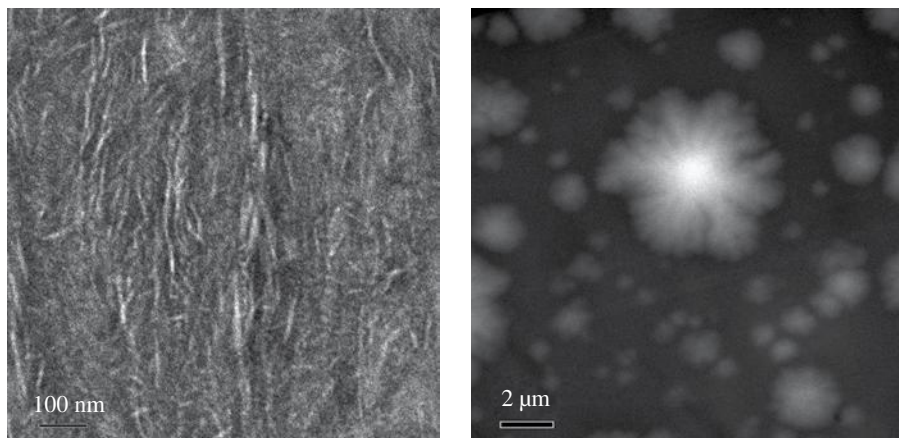


FIGURE 5.6 Illustrative transmission electron microscopy images of polyurethanes. The image on the right is a TEM image of the elastomer shown as an optical image in Figure 5.4. The image on the left shows oriented rodlike hard segments. The orientation is probably an artifact of the compression molding process. Images courtesy of Robert Cieslinski and Justin Virgili. Reprinted with permission from Ref. [33]. © John Wiley & Sons, Inc.

5.2.1.3 TEM TEM is an electron microscopy that has established itself as a very useful tool in polyurethane material science [34]. Like SEM, the sample depends on the interaction of the sample with a thermally or field generated electron beam. Unlike SEM that bounces electrons off of a sample surface, TEM passes electrons through the sample. Since electrons readily interact with materials, the sample must be very thin, on the order of 10s of nanometers thick, to allow sufficient electrons to pass through the sample that a signal can be collected. The image transmitted is a function of the interaction of the electrons with different components of the sample. Although staining is not always required, image contrast can be improved if one phase or another has affinity for a heavy metal contrast agent such as osmium tetroxide or uranyl (uranium) acetate (Fig. 5.6).

The many applications and varieties of use for TEM can be found in resources dedicated to the subject. Among the most critical aspects obtaining a TEM of polyurethane is sample preparation [35, 36] and sampling bias [37]. The need to prepare exceptionally thin samples is complicated by the fact that many urethanes are relatively soft materials resulting in deformation during thin sectioning (microtoming). This may result in the need to perform the microtome at very cold temperatures. However, the utility of TEM for understanding polyurethanes (and for that matter many polymers) has resulted in standardization and commercial instruments able to minimize the complications. Another problem is one of systematic error related to the very small areal coverage of the measurement. This can lead to the search for interesting but rare structures within a sample. It is not uncommon for the rarity of a structure to be lost in the novelty. It is of course the role of the experimentalist to search for representative *and* novel structures. The last issue is the possibility of localized heating of the sample by the beam altering the morphology. This is often visible to the experimentalist and of course should not be ignored.

5.2.1.4 AFM AFM is a relatively recent technology development for imaging materials and has found wide applicability to the study of polyurethanes [38, 39]. Unlike electron microscopies, AFM depends on the interaction of a sample's surface with a scanning tip that can provide an electronic signal to recording electronics or be detected remotely by laser detection off of the tip about its coordinate position and its deflection in the z -position. This obviates the need for large vacuum chambers (although atomic-level detection may still employ high vacuum to prevent gas adsorption). These advantages mean that AFM can be well employed in ambient environments, in solvent-laden systems, or even on biological specimens. Numerous textbooks and research monographs [40, 41] are available with detailed information on instruments and techniques.

When an AFM tip is placed in direct contact with a surface (in essence a measure of the repulsive force), the technique is called "contact mode." Contact mode can be useful for investigating the surface of hard materials. It has the advantage of providing a direct interrogation of the surface but can provide misinformation of surface topology if the surface is deformable by the scanning tip and can also cause tip wear over time, which can affect measurement fidelity. In practice, the tip is scanned over the surface with a constant downward force and the tip position monitored by sensors.

In "noncontact" mode, the tip does not directly contact the surface [42]. Instead, tip position is carefully controlled to hover just above the sample surface. In contrast to the repulsive forces monitored by contact mode, noncontact mode monitors attractive forces between the tip and the surface. The tip is not abraded by wearing on a surface, and the sample surface is not affected by contact with the high-modulus (silicon or silicon nitride) tip. The results of contact and noncontact modes applied to rigid samples will usually be very similar. However, soft materials, or materials with loosely bound surface layers, will be better understood using noncontact techniques. The scanning of the tip over the surface can be operated in a frequency modulation mode where intertip/surface forces modulate at a resonant frequency or can be operated with amplitude oscillation modulation mode where amplitude modulation or phase perturbation can be monitored. These modulations of a controlled frequency or amplitude can be correlated to characteristics of the probed material.

Tapping mode AFM [43] is in some ways a compromise between contact and non-contact methods of tip operation. The tip is oscillated above the surface of the sample, but it approaches the surface much more closely such that it intermittently samples the repulsive or contact regions of the tip/surface interactions. As the material taps the surface, it probes directly the surface topography but does not drag or distort the surface due to lateral surface interactions. Furthermore, the interactions incurred during the taps are readily related to material properties through the sinusoidal phase change induced in the oscillation. Figure 5.7 is an illustration showing a method of tip amplitude control and sample positional control used by one particular manufacturer of tapping mode AFMs.

Figure 5.8 illustrates the portion of the attraction/repulsion potentials sampled by each of these techniques. As the distance of the probe is brought into contact with the surface, the force measured by the probe is greater than zero. This allows a direct measurement of surface topography with position, but may lose information about

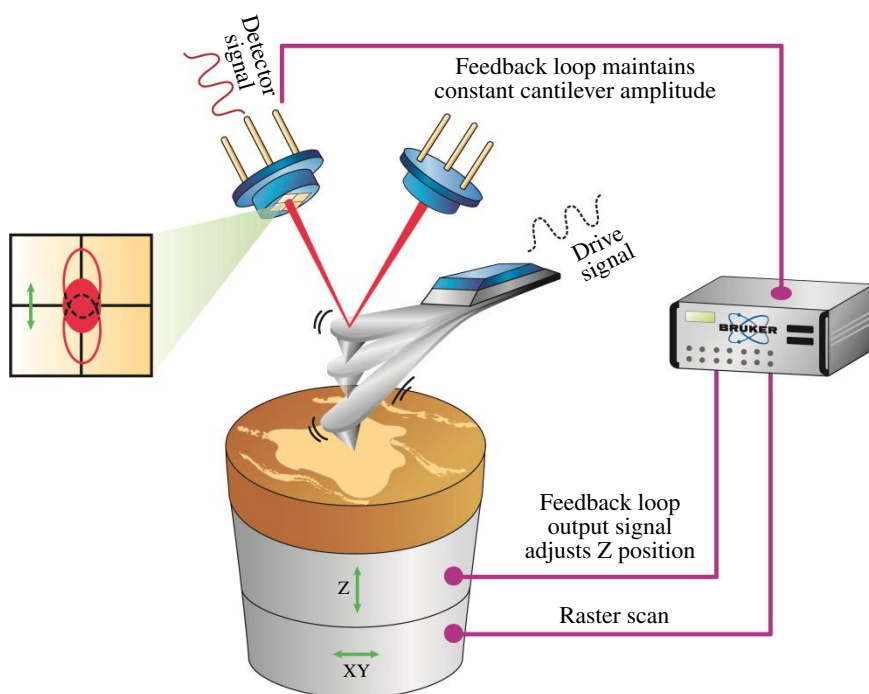


FIGURE 5.7 Simplified illustration showing sample and signal detection controls for a tapping mode atomic force microscope and the appearance of a working instrument. Images courtesy of Bruker Nano-Surface. (See insert for color representation of the figure.)

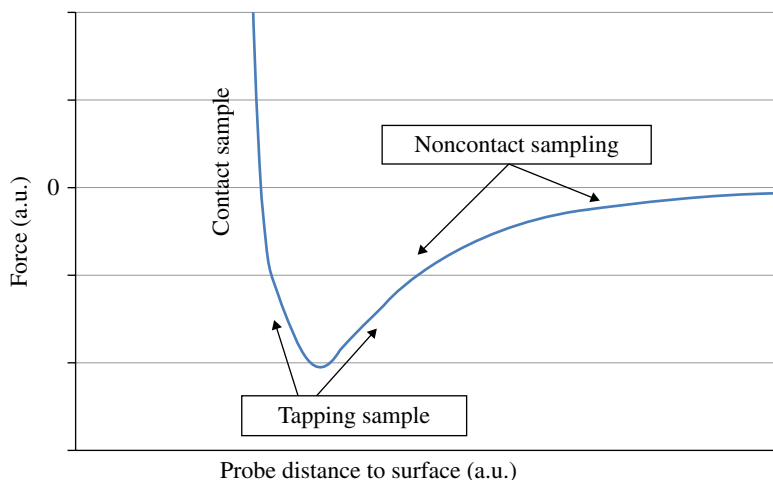


FIGURE 5.8 Potential diagram of attractive and repulsive forces influencing an AFT tip as it approaches a surface in contact, noncontact, and tapping modes.

subtle material properties. It also may suffer some resolution insufficiency if the probe is too blunt to follow acute surface features. In tapping mode, the probe oscillates above but very close to the sample surface. As the probe approaches the surface near the minimum in the force, the attractive forces will bring the probe into physical contact with the surface and bring the measured force into the repulsive region of the potential. This allows the probe to not only sample surface topography but also directly probe material properties such as adhesion and modulus. Noncontact mode samples the region away from the sample surface and samples the positional change in the attractive forces of the material for the probe. As the probe samples the relative height of the sample, it will register as a change in attractive forces.

AFM has brought a new appreciation for the underlying microstructure responsible for the properties of polyurethanes [44–47]. It has furthermore elevated the theoretical basis for understanding the mechanism for polyurethane phase separation and the position polyurethanes occupy as a class of block copolymers [48]. Figure 5.9 is an example of information available from, in this case, tapping mode AFM. The image shows the height image garnered from the potential forces experienced by the probe as it oscillates over the surface termed the “height.” The phase image shows the information obtained by the probe in contact with the surface and as it is preferentially repulsed by the very-high-modulus hard segment (white in the image) and the relatively adhesive soft segment (dark). The image is consistent with proposed theories (see Chapter 4) related to mechanisms of phase separation and block copolymer equilibrium structures. Experimental details are provided in the figure caption to impress upon the reader that even a relatively straightforward experimental technique must be performed with precision and attention to small details to obtain meaningful and useful results. Beyond that, the membrane/lacey structure of the hard segment is remarkable for its aesthetic value as well.

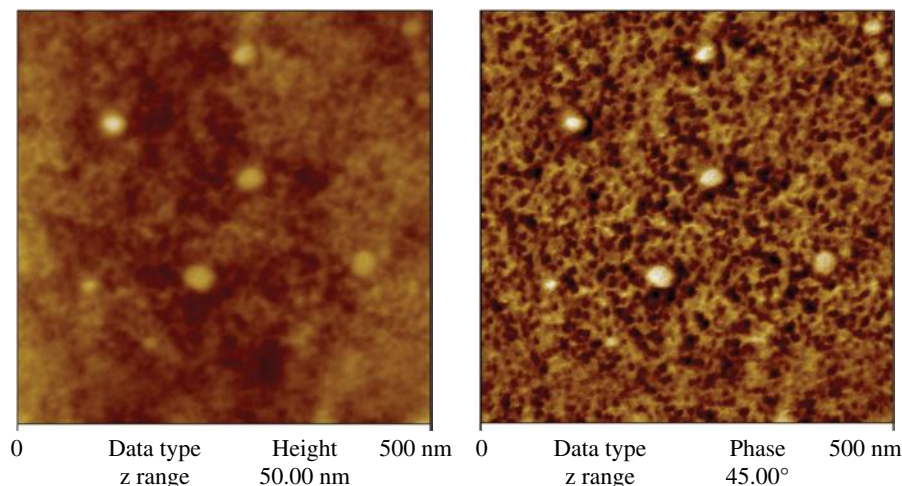
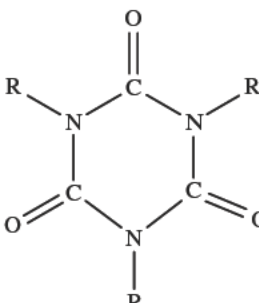
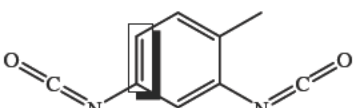
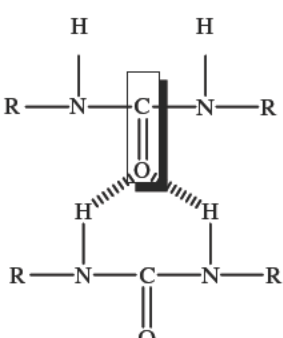
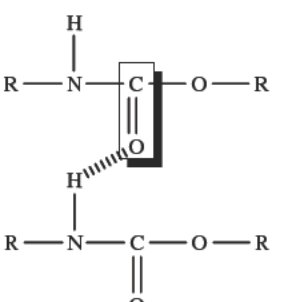


FIGURE 5.9 A piece of the foam was embedded in epoxy and then cured. The cured block was cryopolished at -110°C . The resulting face was exposed to RuO_4 vapor, and then the block was repolished at room temperature. The face on which the TMAFM was done probably had regions that retained the Ru stain. TMAFM was obtained on a Digital Instruments MultiMode using a NanoScope IV Controller (Software v 5.12r3). Silicon cantilevers and tips were used (Nanosensors, LTESP, wafer number 1795L262, frequency = 158 kHz). Typical tapping conditions were $A_o \sim 1.0$ V, $A_{sp} \sim 0.6$ V, and $r_{sp} \sim 0.60$, with the tip/surface interaction repulsive in nature. Images courtesy of Greg Myers. Reprinted with permission from Ref. [44]. © Elsevier Pub.

5.2.2 IR Spectrometry

IR spectroscopy is one of the most widely and successfully applied analytical techniques to polyurethane chemistry and structure [49–52]. The chemistry of polyurethanes is the story of isocyanate and active hydrogen conversion to urethanes, ureas, and isocyanate–isocyanate reactions. During polymerization, strongly IR absorbing functional groups are consumed, and other strongly IR absorbing functional groups are formed. This makes IR spectroscopy particularly useful for following reaction kinetics and perturbations as a function of composition. Table 5.5 is a reference compendium of structures commonly encountered in polyurethane chemistry and associated resonance frequencies. At the same time, the final product structures can exist in various states of interchain interaction, which modify the IR resonances in highly predictable ways. Furthermore, since polyurethanes involve active hydrogen reactants and produce hydrogens in IR-active functional groups, experiments using deuterium isotope affects can be contemplated for information about reaction mechanisms and removing ambiguity in final structures [53]. The systems are also amenable to study by model compounds that can be designed to isolate certain chemical and structural aspects of interest and mitigating confounding or complicating features [54–57]. Lastly, IR measurements are adaptable to other analytical techniques such as X-ray analyses allowing simultaneous measurements of structure formation providing understanding of the order of events, especially phase separation,

TABLE 5.5 Reference for resonance frequencies for functional groups commonly encountered in polyurethanes analysis

Frequency (cm ⁻¹)	Resonant functional group	Structure
1100	Ether	$R - O - R$
1070	Ester	$R' - O - R$
1413, 1710	Isocyanurate	
1598	C=C (TDI ring)	
1640–1645	H-bonded urea in domains	
1695–1700	Free urea	
1700–1710	H-bonded urethane	

(Continued)

TABLE 5.5 (Continued)

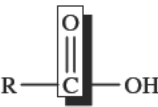
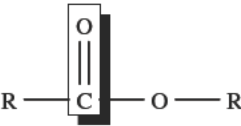
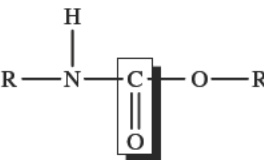
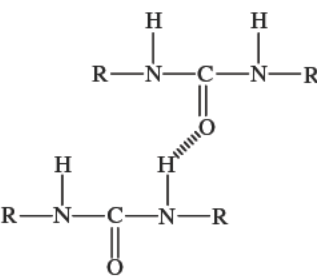
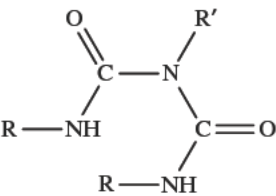
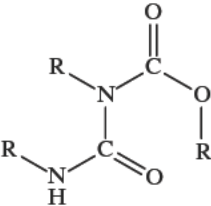
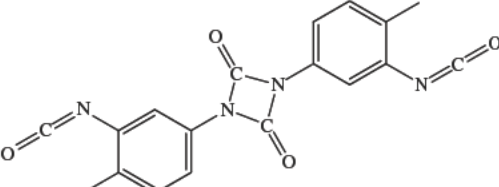
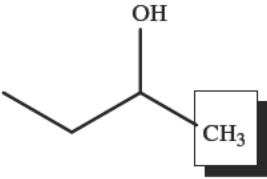
Frequency (cm ⁻¹)	Resonant functional group	Structure
1662	H-bonded urea disordered	
1683	Acid	
1737	Ester	
1730	Free urethane	
1740–1710	Monodentate H-bonded urea	
2100	Carbodiimide	$\text{R} - \text{N} = \text{C} = \text{N} - \text{R}$
2270	Isocyanate	$\text{R} - \text{N} = \text{C} = \text{O}$
1660–1680	Biuret	
1710	Allophanate	
1785	Uretidione (dimer TDI)	

TABLE 5.5 (Continued)

Frequency (cm ⁻¹)	Resonant functional group	Structure
2970	CH ₃	
3200–3500	N–H	
3100–3700	OH	

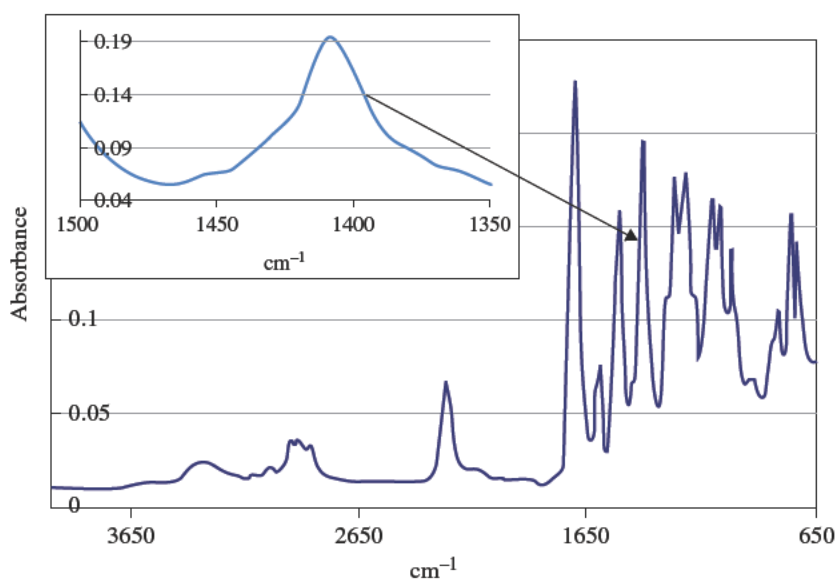


FIGURE 5.10 ATR-FTIR of isocyanurate foam. These foams are made with a significant excess in isocyanate to assure that a large amount of trimer is formed. Isocyanate functionality is clearly visible as an isolated peak at 2270 cm⁻¹. The insert details the IR resonance associated with the isocyanurate ring at 1410 cm⁻¹.

during reaction [58]. Thus, by combining X-ray and IR analyses, polyurethane reaction dynamics can be combined with structural details of the final product.

The power of IR spectroscopy applied to polyurethane chemistry and structure does not imply that reliable data using this technique is easily obtained. Many aspects of polyurethane chemistry hinder obtaining quantitatively reliable data. In the case of polyurethane foaming and foams, the chemistry is very rapid, is exothermic, and involves very large changes in sample density. The product itself is opaque and so is best studied by ATR spectroscopy using Fourier transform instruments. Figures 5.10, 5.11, and 5.12 are examples of foam spectra illustrating interesting resonance features and a complication associated with operating in a transmission versus a surface reflectance mode.

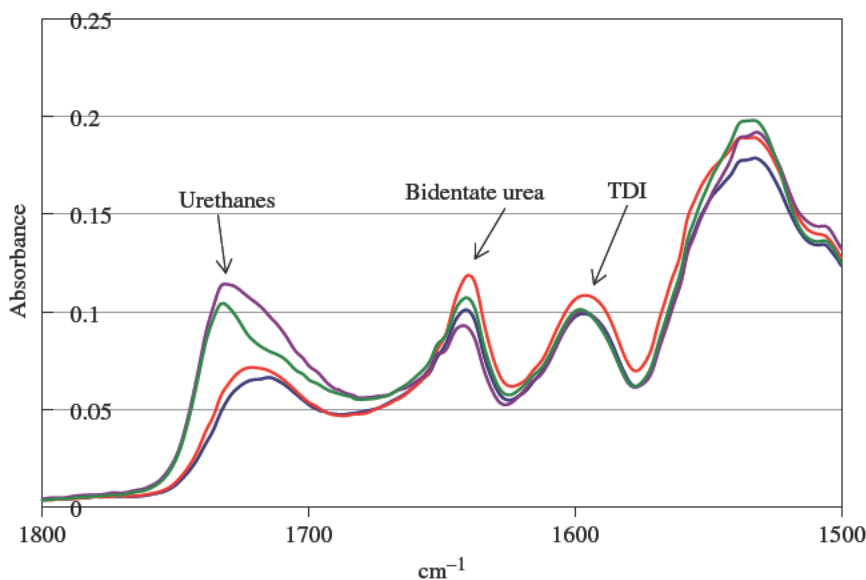


FIGURE 5.11 ATR-FTIR of flexible foams showing the sensitivity of urea/urethane populations of foaming formulation details. The TDI peaks show nearly identical levels of TDI in all 4 foams.

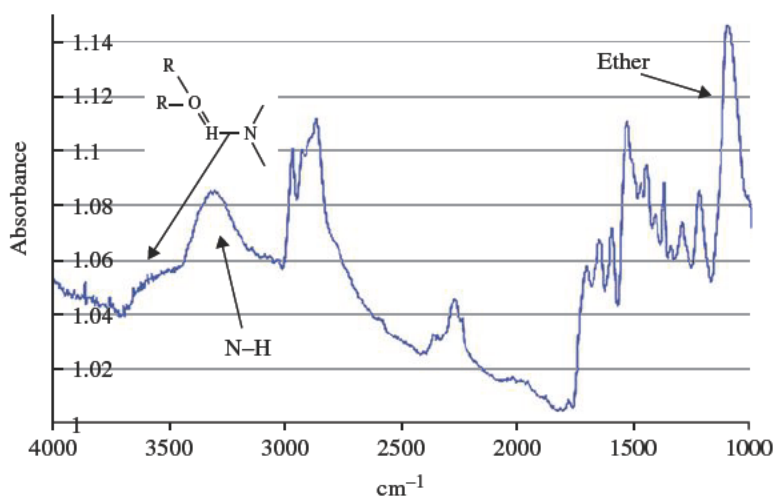


FIGURE 5.12 Transmission FTIR of TDI-PU flexible foam. Notice the difference in absorbance values and baseline offset due to complications associated with working in transmission mode.

5.2.3 X-Ray Analyses

X-ray analysis has become a standard tool for developing in-depth understanding of polyurethane microstructure. It is particularly finding adherents in academic studies of structure–property relationships since scattering techniques can provide unique information on the angstrom to nanometer scale [27, 59, 60]. At this scale, a researcher can learn about packing within the hard segment, the ratio of crystal (or quasicrystalline) to amorphous phase volume, the periodicity of phase spacing, and the characteristics of the interface between the polyurethane soft segment and the hard segment. While X-ray methods are surely complementary to other less instrumentally demanding techniques (such as calorimetry, IR spectroscopy, AFM, and mechanical analyses), X-ray analysis, when done with proper care and control, provides a measurement that requires less inductive reasoning than other techniques applied for the same information. The most basic information provided by X-ray analysis is derived by the very simple Bragg equation 5.6 for determining the interdomain spacing λ , regardless of the intra- or interphase nature of the scattering center:

$$l = 2p/q_m \quad (5.6)$$

where

$$q_m = 4p/\lambda \sin(\Theta/2) \quad (5.7)$$

q_m is referred to as the scattering vector, λ is the wavelength of the incident X-ray radiation (often 1.54 Å for a Cu K_α source), and Θ is the scattering angle. The wealth of additional information contained within scattering diagrams depends on highly involved geometrical reasoning, and obtaining information depends critically on correct application of precise experimental techniques.

5.2.3.1 Wide-Angle X-ray Scattering Wide-angle X-ray scattering (WAXS) is an X-ray diffraction technique used to characterize the crystallinity and characteristic spatial relationships between atoms within a crystalline phase [61]. WAXS spectroscopy is performed with a sample between the X-ray source and the detector. While scattering is strictly from constituent electron density, this is usually well correlated to local density, making it a sensitive probe of local structural variations. WAXS is differentiated from SAXS by positioning the detector closer to the sample so that scattering at wide angles may still be captured. The detector may be a film or digitizing two-dimensional detector such as shown in Figure 5.13. Alternatively, the source may scan an angular range and the detector scan the diffracted intensity as a function of detector angle to provide the so-called 1-D spectrum. Such a 1-D spectrum would be the equivalent of recording the intensity along a single radius extending away from the center of the film to the film's edge.

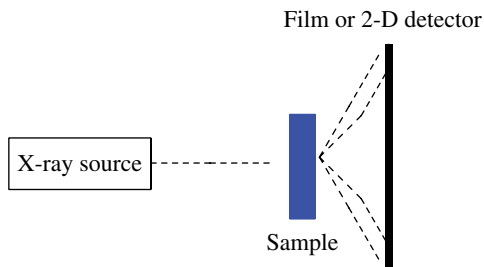


FIGURE 5.13 Relationship of sample to detector for WAXS analysis.

Applied to many polyurethane structures, WAXS is often not particularly enlightening [13, 35, 52, 62, 63]. Since PU hard segment is disordered, sometimes compared to a nematic liquid crystalline structure (like matchsticks in a box), it often results in diffuse scattering. Thermoplastic polyurethanes (TPUs) are particularly diffuse in this regard; however, many TPUs are prepared with glycol soft segments capable of crystallizing. Among these are polybutylene adipate, polybutylene succinate (PBS), and polycaprolactone (see Chapter 2). WAXS of TPUs prepared with crystallizable soft segments may show up convoluted with the diffuse polyurethane hard segment as shown in Figure 5.14. The top image in Figure 5.14 shows a broad diffuse scattering with a well-known peak centered at about $2\Theta = 20^\circ$. A two-dimensional photograph of this pattern would show up as a diffuse halo. Application of the Bragg equation indicates a characteristic scattering reflection of about $4.5\text{ \AA}$. Progression of the sample shows that as design of the TPU is adjusted to encourage soft segment crystallization, the characteristic scattering from, in this case, PBS diol appears and begins to dominate the diffraction pattern.

The polyurea hard segment scattering emanating from polyurethane foams can show a greater amount of ordering and more reflections than observed for TPUs. This is as might be expected given the higher ordering power of the bidentate hydrogen bonding within the polyurea hard segment. Figure 5.15 is a representative WAXS from a water-blown foam. In this figure, the characteristic $2\Theta = 20^\circ$ is prominent as well a shoulder at about $2\Theta = 10^\circ$ and 50° . A two-dimensional image of this pattern would show a less diffuse scattering intensity than observed in Figure 5.15 with sharper intensity maxima (still showing circular symmetry in the image) at the indicated 2Θ distances. The exact morphological nature associated with the scattering is not established but is believed to be characteristic of the hard segment hydrogen bonding network inferred from the commonality of many of the reflections independent of whether the isocyanate is MDI, pMDI, or TDI [35]. In principle, processing variations such as compression molding, injection molding, annealing, etc. could affect WAXS patterns, but in practice, this is rarely observed. Soaking PU samples in strong solvents is known to decrease or even eliminate some of the WAXS, but this is certainly unsurprising. Large-scale sample deformation has been observed not to change peak maxima, but rather, in some cases, to change the overall peak shape [66].

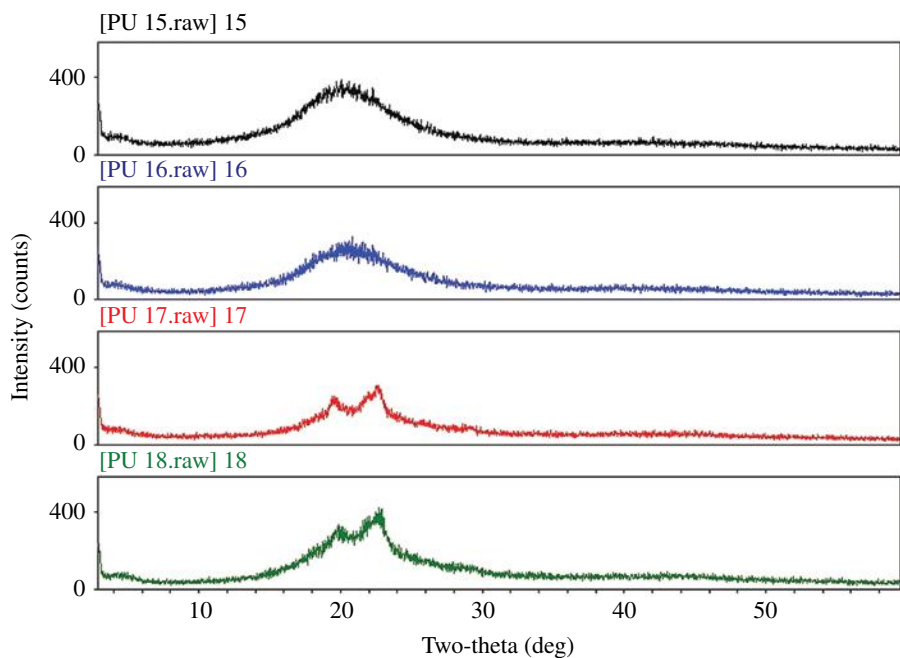


FIGURE 5.14 WAXS data for polyurethane elastomers with polybutylene succinate (PBS) soft segments and MDI-BDO hard segments. As conditions are optimized for soft segment crystallization, the PBS diffraction becomes more prominent in the data. Reprinted with permission from Ref. [64]. © Elsevier Pub.

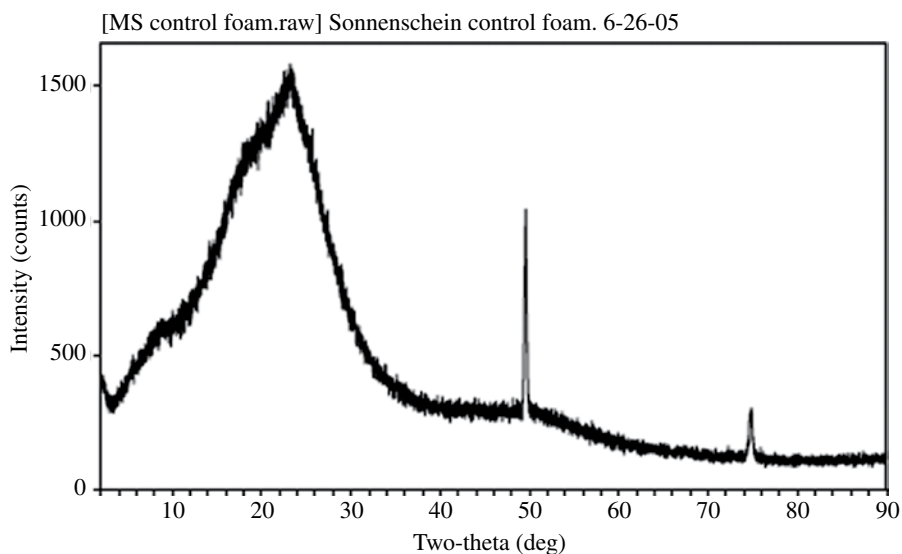


FIGURE 5.15 WAXS from a polyurethane foam with a polyurea hard segment. Reprinted with permission from Ref. [65]. © Elsevier Pub.

5.2.3.2 SAXS Application of SAXS alone and in concert with other techniques, such as WAXS, rheology, FTIR, and others, has provided powerful insights into polyurethane formation and structure [67–72]. The broad concepts related to SAXS are quite similar to those of WAXS [73, 74]. The detector is moved quite a bit farther from the sample than in a WAXS experiment, on the order of 0.5 m to more than 3 m when employing synchrotron radiation sources [63]. Wide-angle scattering signal is not detected or is faintly registered by the detector. Instead, only the scattering at low angular dispersion from the main beam intensity is recorded. Low-angle scattering detection results in the need to have good removal of the main beam (and other background sources as will be discussed later) to obtain the most useful and interesting information. A means of removing this direct beam intensity is shown in Figure 5.16 where a physical beam stop is employed. The passed scattered intensity will fall upon the detector representing the amplitude of the Fourier transform of the shape in the beam. Polydispersity of the size and shape of randomly oriented scattering objects, as usually exist in polyurethanes, results in a superposition of scattering patterns leading to a smooth function such as shown in Figure 5.17. Alignment of nonspherical scattering objects can lead to anisotropic scattering patterns. Interpretation of scattering using classical analyses involves fitting the measured scattering to models based on polydisperse known shapes such as spheres [75]. The modeling and interpretation become more challenging as complex shapes must be accounted for. From the fit of data to models, insightful information on the spatial distribution of particles in the sample, their potential agglomeration, their interfacial characteristics, and their shapes can be obtained [76].

The center of the scattering peak is indicated in Figure 5.17, and the calculated d-spacing showed based on the Bragg equation given by Equation 5.6. The d-space quantity is of interest by itself in polyurethane science, since it is a quantitative measure of the interhard segment spacing that can then be correlated to various formulation and processing variables. It should be pointed out that d-spacing based on picking out the center of the first peak can sometimes be

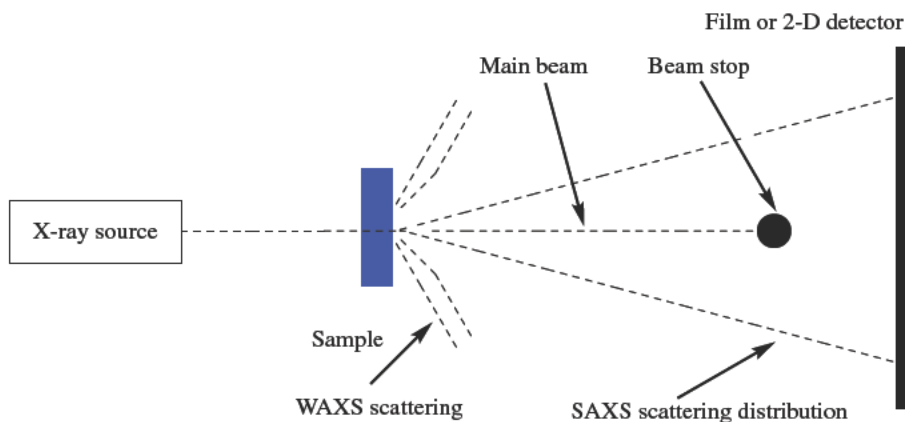


FIGURE 5.16 Relationship of sample to detector for SAXS analysis. Compare to Figure 5.13 for WAXS analysis.

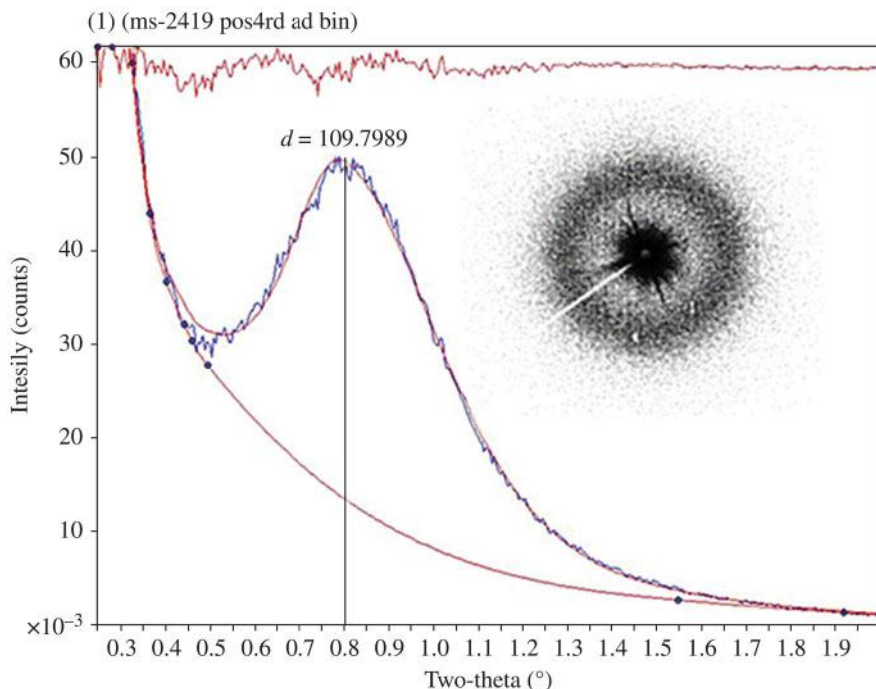


FIGURE 5.17 SAXS data for a polyurethane foam. Inset is the 2-D data.

fairly easy as in the pattern of Figure 5.17. Other times, as will be shown in the following text, picking the peak intensity will be imprecise enough that a d-space calculation will be best characterized as an estimate. Data analysis techniques can be employed to improve the accuracy and precision of the d-space calculation. One such correction is the Lorentz correction for removal of vestigial main beam intensity. This technique is appropriate for lamellar scattering structures, which many polyurethane hard segments are, but certainly not all. Systematic control of variables and careful analysis of data can then allow for improved understanding and prediction of polyurethane properties. Furthermore, it has been demonstrated that simultaneous measurement of the growth of SAXS with rheological, spectroscopic, and thermal properties can provide new insights into polyurethane structure and property development [51].

The fact that scattering is a function of geometry and that ideal shapes scatter X-rays in well-understood ways has provided additional opportunity to understand polyurethanes for the frequent instances where ideal response models do not perfectly fit. The variance with expectations can be modeled and the closeness of fit to data used to provide additional structural insights that can be tied to polymer properties. Among the most useful models is based on the theoretical analysis by Porod on deviations from ideal scattering behavior due to the real interfacial thickness of phase separated systems [77–79]. These interfacial thicknesses are also referred to as boundary widths or diffuse boundary thicknesses.

It is vital to note that the Porod analysis requires that for a 2-phase system with a perfectly sharp interface, the long q values must decrease according to an inverse 4th power:

$$\lim_{q \rightarrow \infty} [I(q)] = \frac{K_p}{q^4} \quad (5.8)$$

where K_p is a constant defined by Porod as

$$K_p = \frac{Q}{2\pi^3 I_p} \quad (5.9)$$

In Equation 5.9, I_p is the Porod inhomogeneity length and Q is a term described variously as the “invariant” or the “Porod invariant” defined explicitly by

$$Q = 4\pi \int_0^\infty q^2 I(q) dq = V \varnothing_1 \varnothing_2 (\rho_1 - \rho_2) \quad (5.10)$$

K_p can also be calculated as the limiting value reached by the product of $I(q)q^4$. In Equation 5.10, $\varnothing_1$ and $\varnothing_2$ are the volume fractions of the respective two phases and ρ_1 and ρ_2 are the respective electron densities.

It is in the variation of data from expected ideal values that interpretation of polyurethane structure can be understood and properties systematically refined. In the cases where $I(q)q^4$ does not reach a limiting value, the inferences can be particularly illuminating. In polyurethane research, the usual case is for a graph of $I(q)q^4$ versus q^2 to have a negative slope. This result can be interpreted as a result of diffuse phase boundaries (as opposed to a very sharp phase boundary) and phase mixing [80]. The result of the phase mixing is a depletion of scattering intensity at high scattering angles that are more closely associated with the region closest to each scattering center and less with the regions between the scattering centers [81, 82].

As seen in Figures 5.17 and 5.18a, the scattering intensity at high values of q is small and declines rapidly (at or near the 4th power) as predicted by the Porod analysis. Thus, the means of subtraction for background intensity, beam collimation, and even vestigial wide-angle scattering is critical to obtaining unbiased reliable results. In a critical review of correction techniques, it has been shown by Koberstein et al. [76] that representation of the background correction as a constant will always lead to overestimation of interfacial mixing. This is due to overestimation of the decline in background intensity that leads to an exaggerated negative deviation from ideal expectations based on the Porod analysis.

Obtaining the correlation function of scattering requires calculation of the Fourier transform of the one-dimensional SAXS curve [83, 84]. This yields a curve of γ_1 termed the correlation function that is the spatial correlation of the electron density correlations. A useful mental image is to imagine the function $\gamma_1(r)$ as the probability of scattering from a rod of length r with equal electron densities at either end. A peak

in the resulting correlation function will then occur when there is a frequently occurring spacing within the structure. An example of SAXS and the resulting correlation function is given in Figure 5.18. The first peak in the correlation function represents the d-space distance that would normally be estimated from the peak in the scattering intensity. In the provided example, picking out a maximum may not be a particular challenge, but there are many examples where defining a d-space could be somewhat more challenging or arbitrary as shown in Figure 5.19. Features of the correlation function can lead to direct calculation of various useful quantities related

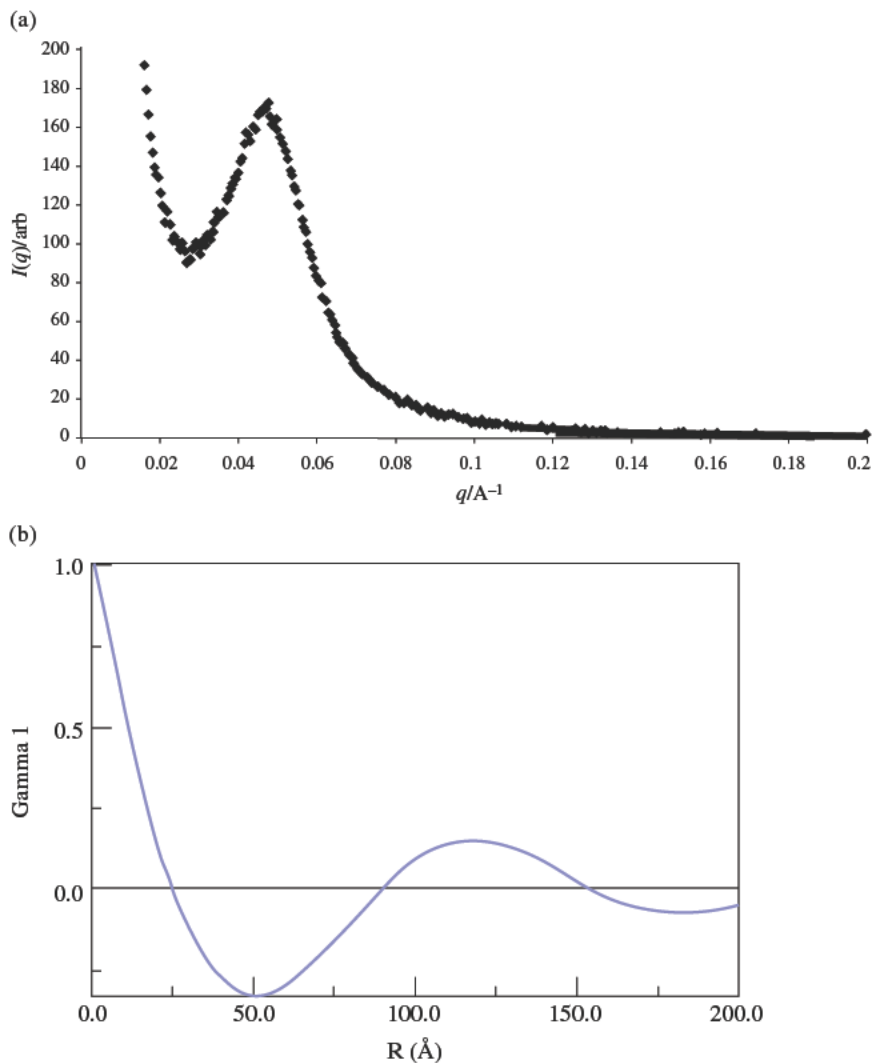


FIGURE 5.18 SAXS data for a molded polyurethane foam and the derived correlation function. (a) SAXS data for a molded polyurethane foam and (b) the derived correlation function. Reprinted with permission from Refs. [44] and [65]. © Elsevier Pub.

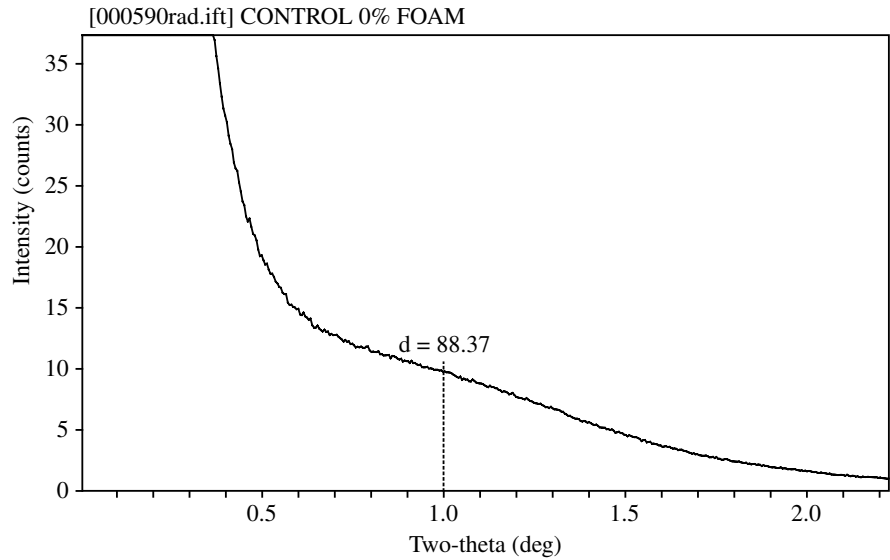


FIGURE 5.19 SAXS data for a TDI-flexible slab foam. The d-spacing determination requires more judgment that required for data such as Figure 5.17.

TABLE 5.6 Data derived from a porod analysis of Figure 5.17

d-spacing Å	118
L_H hard block thickness Å	26.3
L_S soft block thickness Å	91
ϕ_v bulk volume crystallinity	0.23
ϕ_H local crystallinity	0.22
σ interface thickness Å	3.0
Polydispersity	0.23

to the 2-phase structure, the values of which can be used to determine the relevant structure–processing–property relationships of polyurethanes. An example of such data is provided in Table 5.6, which gives available phase information from the scattering pattern and resulting correlation function of Figures 5.18.

5.3 MECHANICAL ANALYSIS

The mechanical analysis of polyurethanes is a very broad topic, and it is difficult to cover in depth without a companion discussion associated with 2-phase composite theory and the theory of block copolymers, which are covered in Chapter 4. However, most measurements associated with the performance of a specific polyurethane in a

particular application begin with some kind of mechanical analysis. This is obviously true when one considers that a polyurethane foam must function under compression, an elastomer under compression or tension, an adhesive under tension or shear, a coating under complex wear processes and chemical insult, and so on. Certainly, techniques such as X-ray scattering or spectroscopy may provide in-depth understanding of how or why a polyurethane structure exists. They do not, however, provide a predictive measure of how that particular structure will perform in a lap shear test, how long the structure will elongate under a particular load, or how much permanent set the structure will exhibit when sat upon in July in a humid or dry environment. For this information, there are few substitutes for well-thought-out tests of mechanical performance. The fact is that whether for foams, adhesives, elastomers, coatings, sealants, or any other imaginable application, the specific mechanical tests are often very unique to the industry or even customer. The ASTM has numerous tests with specific methods for testing. Many tests such as those covered in Section 5.1 are well used and truly applied across industry and academia. Mechanical testing is handled differently because of regional differences in application requirements (i.e., Northern Europe vs. South America) or because of historical testing protocols that predate standardized methods. Some tests simply reflect the biases of material scientists represented within a certain company. In this section, there will not be an attempt to cover all the tests that exist. This could probably fill a book in itself and would represent a moving target as test requirements can change rapidly. Rather, this section covers mechanical testing of materials in large strain (displacement) modes such as occur in tensile, tear, and elongation tests and in small strain modes such as that occurs in DMA. These tests each provide very useful and different information on material properties. In addition, DMA can be employed to provide information on reaction kinetics, rheology, frequency, and temperature-dependent properties of materials—but only at relatively low strains.

5.3.1 Tensile, Tear, and Elongation Testing

As indicated earlier, many application tests are specific to the application and even the customer. Many of these unique standard tests are modifications of ASTM tests. Some relevant ASTM tests are listed in Table 5.7.

For tensile, tear, and elongation information [85], the workhorse piece of equipment is an instrumented tensile testing machine. Such machines are made by several purveyors including Instron Corporation and MTS Systems Corporation. These machines are essentially rectangular frames. Samples are positioned within the frame using specially designed fixtures. The fixtures are made to insure that meaningful and reproducible results can be obtained according to precepts of good mechanical engineering and physics. Attached to one end of the fixture is a device called a load cell, which is essentially a device that measures force. Stress is obtained from the force measurement by normalizing to a geometrical factor such as sample cross-sectional area. At the beginning of a test, the top or bottom end of the frame will move relative to the other three sides of the rectangle applying stress to the sample. The stress is recorded by the load cell much as a scale will measure weight upon standing

TABLE 5.7 Conventional polyurethane mechanical tests and ASTM procedures for measurement

Property	ASTM test and comments
Tensile properties of plastics	D638 for reinforced and unreinforced plastics (not carbon fiber composites) includes test for measuring Poisson's ratio at STP
Test methods for vulcanized rubbers and thermoplastic elastomer—tension	D412 overlaps D638 substantially but also covers a nondumbbell/rectangular geometry and unrecoverable set measurement
Standard test method for slab, bonded, and molded cellular polyurethane foams	D3574 includes method of sampling, indentation and compressive force, tear, airflow, dynamic fatigue, humid/wet aging
Standard specification for flexible polyurethane foams for furniture seating, bedding	D3453 guidance for acceptability and applicability for PU furniture uses
Standard methods for microcellular foams	D3489 overlaps in many ways with other specifications for foams
Standard test method for abrasion resistance-static sample w/ moving abrasive	D1630 uses a standard testing machine executing a controlled abrasion of a stationary test sample against an abrasive paper
Abrasion resistance—moving sample and a moving abrasive	D5963 standard rotary drum abrader corresponds to the DIN Abrader standard test 53516
Rubber resilience by ball rebound	D2632 vertical rebound resilience test ratio of drop height to rebound height of standard plunger. Correlates to tan delta value at temperature
Elastomer deterioration by repeated flexure at application specified temperature	D1052 cut growth by Ross flex test for footwear. The test specifies STP conditions, but many footwear applications demand conditions of 300,000 flexures at -15°C
Hardness testing	D2240 durometer measurement using standard indenters spanning specific ranges of hardness. Correlates to polymer modulus
Compression set	D395 compression of a standard disk by a specified amount and amount of recovery. Although the test specifies STP conditions, it is normally performed at elevated temperature or humidity conditions to gauge polyurethane network stability
Hydrolytic resistance	D3137 and D573 specific test for effect of distilled water for a given time (i.e., 96 h) at elevated temperature (i.e., 85°C). Test can be run at buffered pH levels as well. Applies particularly to systems with polyester soft segments due to susceptibility to hydrolysis

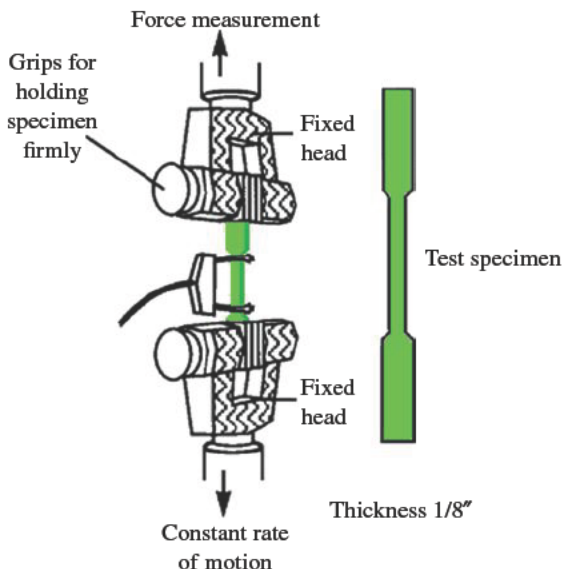
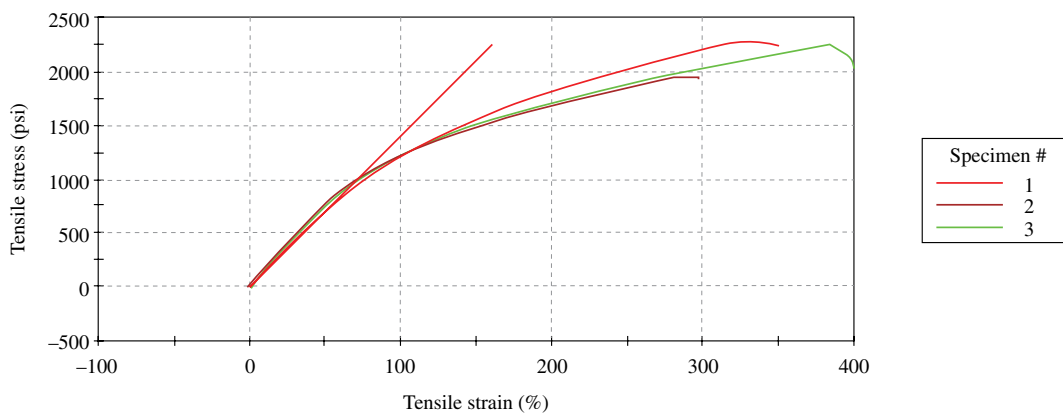


FIGURE 5.20 Illustration of conventional tensile measurement configuration. Stress on the sample can be applied from either top or bottom, and the load cell measuring force can also be above or below the sample depending on the instrument manufacturer.

upon it or hanging a weight on the end of a spring. Figure 5.20 shows a diagram for a standard fixture for tensile measurements.

Representative stress–strain tensile data for a polyurethane elastomer and calculated output is provided in Figure 5.21. The instrument is capable of providing frequent sampling of the load cell reading with time such that the data presentation is smooth and does not show significant loss of resolution due to time averaging. The tangent straight line in the image is a computer-drawn measure of the tangent to the initial part of the stress–strain curve termed the modulus. The slope at different strain intervals can also be captured and compared to the initial readings. In addition to the slope of the curve at any given interval, the data analysis can determine the ultimate elongation, the tensile strength (the maximum stress achieved by the sample), the ultimate strength (the stress achieved at the sample break), the toughness of the sample (the integral under the stress–strain curve), and numerous other tensile parameters.

Polyurethanes are unique in their versatility. They can be used effectively in almost any potential application and that application will usually have a tensile fixture with explicit mechanical engineering so as to provide the most useful and accurate information. Figure 5.22 shows example fixtures designed specifically for application testing. Each fixture takes into account maintenance of correct angles, mechanical compliance, and mass so that the loads to be measured are correctly matched to the load cell capability [86]. In this regard, one would not want to test the compressive properties of a low-density foam specimen with a load cell used for compression of dense elastomers where the modulus can differ by orders of magnitude.



	Specimen label	Modulus (automatic) (psi)	Modulus(young's 0.63 mm-1.64 mm) (psi)	Maximum tensile stress (psi)	Tensile strain at Maximum tensile extension (psi)	Maximum tensile strain (%)	Modulus (Segment 5% -25 %) (psi)	Maximum tensile stress absolute peak (psi)
	1 40% HS 28-1-49 NOP-TPU-A	1352.46	1530.96	2236.470	351.1169	351.11687	1443.00	2268.822
	2 B	1555.93	1862.76	1924.997	297.7810	297.78100	1713.48	1957.163
	3 C	1412.35	1660.77	2029.442	399.9983	399.99831	1588.47	2245.898
Mean		1440.25	1684.83	2063.636	349.6321	349.63206	1581.65	2157.294
Median		1412.35	1660.77	2029.442	351.1169	351.11687	1583.47	2245.898
Standard Deviation		104.56634	167.20399	158.52715	51.12483	51.12482	135.36937	173.69741

FIGURE 5.21 Representative stress–strain data for polyurethane elastomer sample and example of data output.

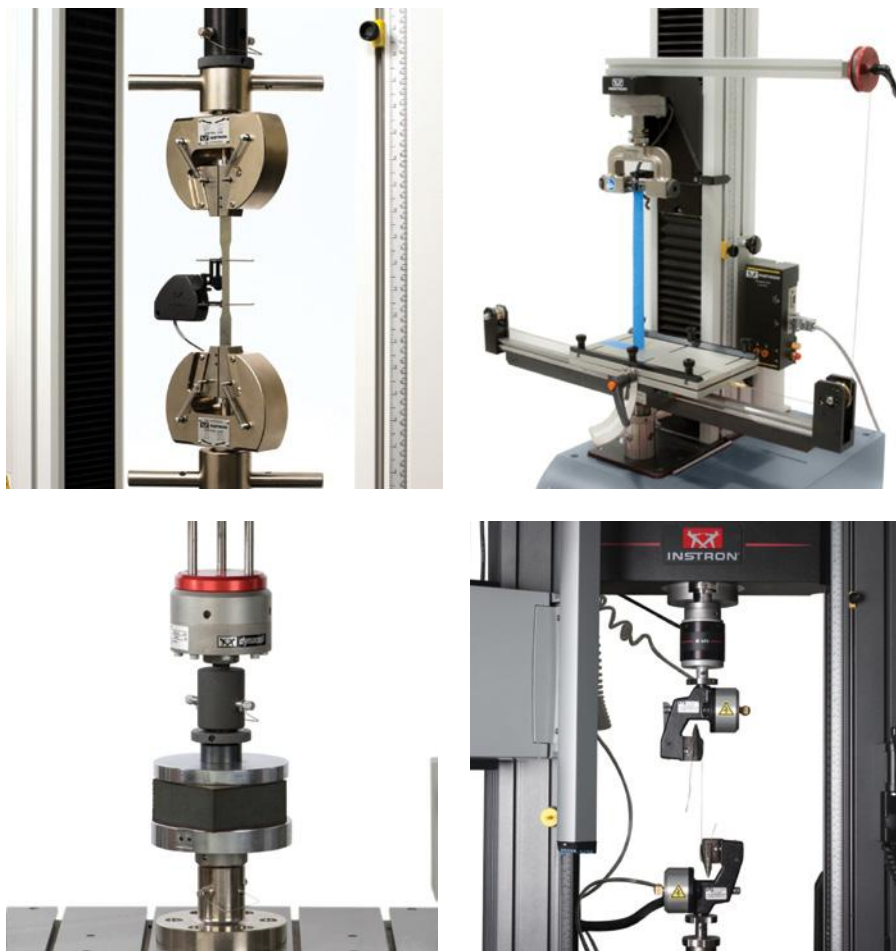


FIGURE 5.22 Useful fixtures for mechanical testing of polyurethanes. Clockwise from upper left: standard tensile fixture for testing plastics, 90° peel test fixture, cord and yarn fixture, and compression fixture. Images courtesy of Instron®. (See insert for color representation of the figure.)

Software for obtaining information from stress–strain experiments is generally provided by the instrument vendors. The software available is highly advanced and becoming ever more intuitive in its user interface. It is in the correct use and setup of the individual test from which information is obtained that differentiates the quality of results. To optimize results, one must use the equipment such that the load cell measuring force is in the correct range of the measurement (for instance—not measuring 50 g of force with a 5000 kg load cell), using fixtures that are correctly sized, aligned to the sample and do not damage the sample such that the grips predispose the sample to failure, correct measurement of extension, and performing the

experiment at an appropriate extension rate. There are clearly a large number of things to keep in mind, and there is no substitute for training and experience. Figure 5.23 shows a typical tensile testing device in use. The fixtures in this case are those used for measuring the tensile properties of a film. The fixture is optimized to minimize damage to the film while at the same time providing a firm grip on the sample ends.

A common fixture for measurement of elastomer properties is that shown previously in Figures 5.20 and 5.22. In this case, the sample is formed such that the ends are wider, providing additional gripping surface by the hydraulically actuated flat or serrated grips. While the sample geometry is well known and widely used, a common artifact with this geometry occurs when the sample yields and draws material for extension from the wide sample ends. A device called an extensometer (depicted in the diagram) is sometimes employed to provide a true measure of sample extension within the narrow sample zone meant to be studied.

An example of the design concepts in the fixtures is shown in Figure 5.22 showing a fixture designed for testing a pressure-sensitive adhesive-type material. One can see that the fixture is designed to maintain a draw angle of 90° with respect to the adhered surface, and this is maintained by a pulley system that draws the adhered surface an amount equal to the length of adhesive pulled. The adhered surface and the drawing grip have sufficient stiffness that they do not vibrate or distort the signal representing the force of pulling the adhered surfaces. At the same time, the fixture, particularly the grip, is low mass and does not require the use of a large load cell in order to allow a tare or zeroing of the measured load prior to beginning the draw experiment. Similarly, the foam compression fixture is a low mass and high stiffness design allowing for easy centering of the foam sample between the compressing platens.



FIGURE 5.23 A technician measuring a film sample using a tensile testing machine.

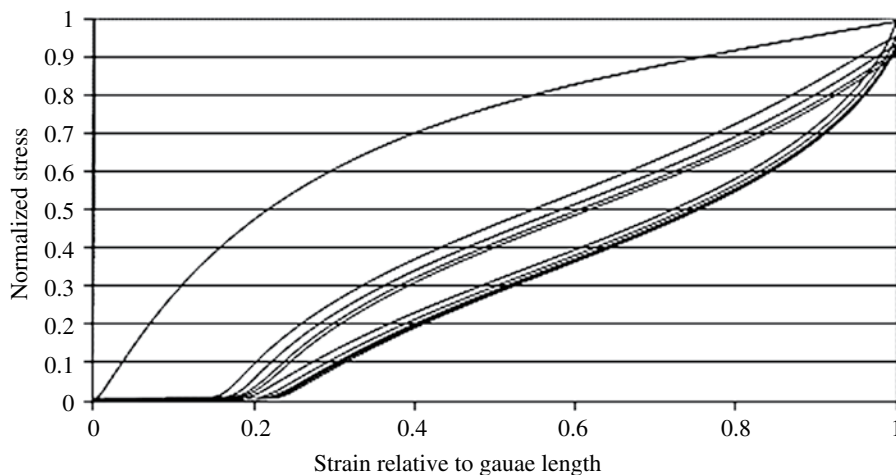


FIGURE 5.24 Hysteresis loop of a polyurethane elastomer with 45% hard segment.

An additional experiment often applied to polyurethane elastomers and flexible foams is the hysteresis measurement [87]. This is a cyclic loading–unloading experiment in which the sample is extended to a set fraction of gauge length (usually 100 or 300%) and the crosshead lowered back to the original gauge length. It is clear from Figure 5.24 that the sample has reached zero stress prior to the crosshead reaching its original position. This is an indication that the sample does not relax as fast as the crosshead was lowered and may have been permanently distorted. The sample is subsequently extended again. From its distorted state, with a longer length and polymer changes having occurred on the molecular level, the material does not achieve the same stress state on subsequent pulls. In general, it is deemed desirable for the area encompassed within the loop be as small as possible (having low hysteresis), which would suggest a high degree of network connectivity and fast chain relaxation processes. A typical hysteresis experiment will often comprise three or five loops trying to achieve unchanging hysteresis during the stress–strain loop.

5.3.2 DMA

DMA or dynamic mechanical spectroscopy (DMS) is a means of measuring the viscoelastic properties of a material, the rheokinetics of a reacting material, or the rheology of a simple or complex fluid [88]. DMA's versatility has made dynamic mechanical analyzer use in polyurethane science very widespread, and it is certainly one of the most useful pieces of equipment in characterizing polyurethanes. Unlike a tensile test, the materials tested by DMA are rarely if ever tested intentionally to a failure condition. Instead, the sample is subjected to an oscillating or sinusoidal strain around a zero strain or a zero reference point. A so-called strain sweep is usually performed prior to a full analysis to make sure that the applied strain does not exceed the linear elastic limit of the material nor the force limits of the load cell. This is similar to maintaining the strain in the

very-low-strain conditions found at the beginning of a tensile measurement. If the experimentalist were to exceed these linear viscoelastic conditions, the material would permanently deform, and the measurement would not have a clear reference condition. Strains are often on the order of 1% of the gauge length (distance between grips) or a few degrees relative to a full 360° twist of the material, depending in each case on the thickness and hardness of the material being tested. An experimentalist will likewise often perform a frequency sweep of the material prior to beginning a full material analysis. This is to assure that the material properties are not significantly sensitive to the frequency of the applied sinusoidal strain. A frequency-sensitive material, or a material near a rheological event like a glass transition, may show a frequency-dependent modulus, for instance. This frequency/temperature conflation is a process called time-temperature superposition and is well understood [89]. Problems associated with this condition in a frequency experiment like DMA are easily avoided through good laboratory practice. A typical frequency is 1 Hz unless the point of the test is to explore the frequency dependence of the material (which is a common enough experiment). The conditions of the constant strain experiment apply to a rotational stress applied to a disk-shaped object in compression or a torsional stress applied to a rectangular object in tension. In both cases, a set of minimal force in compression or tension is applied to assure fixture contact or sample rigidity, respectively, and the sinusoidal strain and measured force measured against this initial “zero force” reference condition.

Alternatively, a constant sinusoidal stress can be applied to the sample and the resulting induced sample strain measured. This is a less common experiment than the constant strain experiment. In principle, the stress is defined by the strain and the strain defined by the stress; however, particularly, in the case of polyurethanes, this expectation is rarely if ever realized.

The mechanical analysis of viscoelastic materials is derived from the definition of mechanical properties in these experiments. As oscillation proceeds, the material stress (i) increases with strain, (ii) decreases as the material is returned to its zero strain state, and then (iii) increases again as the material is strained in the opposite direction from the first oscillation. For a perfectly elastic response, there is no energy lost within the material during the cycle, and the modulus of the material is given by

$$E' = \sigma / \varepsilon \quad (5.11)$$

where E' is the so-called storage modulus of the material or the energy put into the material that is immediately available to be returned, “ σ ” is the applied stress, and “ ε ” is the applied strain (the use of Greek letters is conventional in this field). In a viscoelastic material, E' represents the elastic component. Most nonideal materials such as polyurethanes will not be well represented by this equation as there are numerous molecular processes that can occur capable of dissipating some of the energy put into the sample during the stress phase of the experiment. In these oscillating experiments consisting of elastic energy storage E' and energy losses E'' due to viscous processes, their moduli are defined by

$$E' = \frac{\sigma_0}{\varepsilon_0} \cos \delta$$

$$E'' = \frac{\sigma_0}{\varepsilon_0} \sin \delta$$
(5.12)

The ratio of the loss modulus (E'') to the storage modulus is termed the $\tan(\delta)$ (called the “tan delta”):

$$E''/E' = \tan(\delta)$$
(5.13)

The $\tan \delta$ is the phase lag between applied strain and measured stress, a very sensitive function of phase transitions. Representative data obtained from a DMA experiment on a polyurethane elastomer is shown in Figure 5.25. Figure 5.25b is the

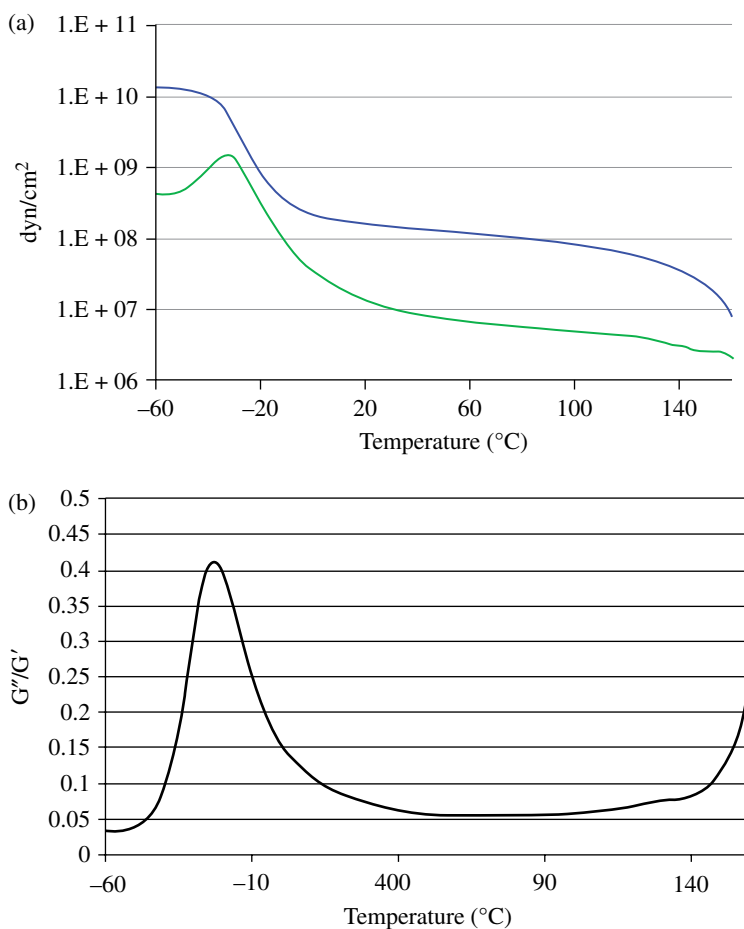


FIGURE 5.25 Representative DMA for a polyurethane elastomer: (a) storage and loss moduli and (b) $\tan \delta$ spectrum—the ratio of loss divided by storage modulus.

$\tan \delta$ spectrum for this elastomer clearly showing the glass transition temperature (the peak with maximum at -25°C in this case) and the onset of urethane reversion (see Chapter 3) beginning about 120°C .

More than 70% of all polyurethane chemicals are processed into foams. The DMA spectra of these materials have been shown to be very similar if not identical to the underlying elastomer except exhibiting a much lower modulus reflecting the well-known squared dependence on density [90]:

$$\sim \left(\frac{E_{\text{foam}}}{E_{\text{solid}}} \right) \sim \left(\frac{\rho_{\text{foam}}}{\rho_{\text{solid}}} \right)^2 \quad (5.14)$$

Experiments on foam samples are ordinarily done on disk-shaped samples. Examples of DMA fixtures for shear and torsional experiments are shown in Figure 5.26.

DMA experiments can also be employed to provide time- or temperature-dependent rheology for reacting systems. In this case, the components of the reaction are introduced into a cuplike fixture and a plate attached to the load cell submerged into the reacting components. The plate will oscillate through the reacting mixture measuring the growth of molecular weight as an increasing resistance to plate rotation. Since the forces are often low in the initial state, the plate usually must oscillate with relatively higher amplitude through the mixture. A typical DMA in use is shown in Figure 5.27 and the data obtainable from a rheokinetic experiment in Figure 5.28.



FIGURE 5.26 DMA fixtures: (a) parallel plate fixture for measurement of thin solid samples in shear or reacting liquids and (b) torsion fixture for measurement of solid sample viscoelastic properties. Fixtures are carefully engineered and machined to provide minimal compliance and minimum mass. Images courtesy of TA Instruments. © 2013.



FIGURE 5.27 A technician preparing a DMA for analysis using a cup and plate fixture.

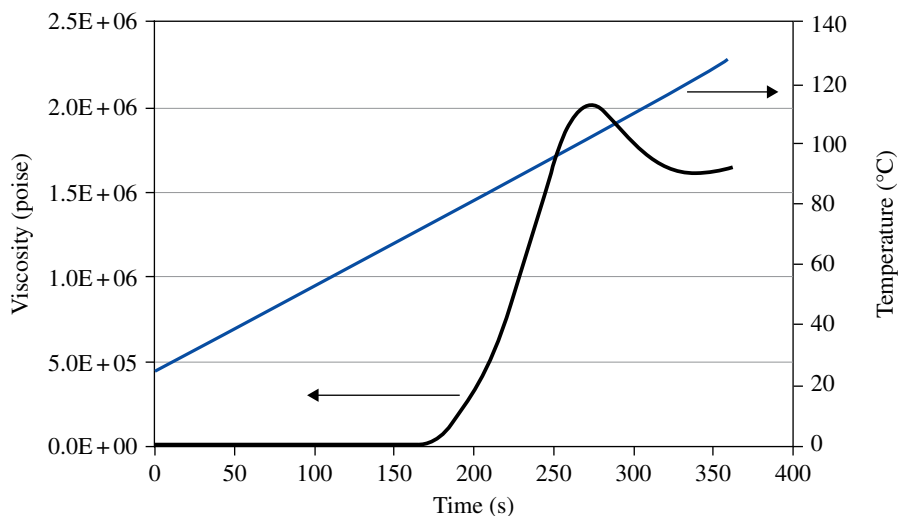


FIGURE 5.28 Example of rheokinetic data obtainable with DMA for a 2-part reacting system like a polyurethane.

5.4 NUCLEAR MAGNETIC SPECTROSCOPY

Nuclear magnetic spectroscopy (NMR) is an analytical technique that has been around for a relatively long time. However, apart from conventional chemical analyses, its application to polyurethanes and polymer structure has lagged other methods due to the technical difficulties associated with NMR of solids [91]. The basic

concepts of NMR of liquids apply to the NMR of solids generally and polyurethanes specifically. They are well covered in numerous other references [92, 93]. In the solid state, the number of interactions of any nucleus with its environment (i.e., dipolar, quadrupolar, j coupling, etc.) is very inhomogeneous and has a time dependence resulting in highly diffused resonance absorption frequency. The advent of magic angle spinning (MAS) techniques has allowed for narrow resonant peak measurements to be made on solid polymers, which would normally be too broad [94–96]. MAS spin rates are on the order of 5–10 kHz, and the magic angle of the sample placement in the magnet is 54.74° . The advent of MAS techniques has allowed for measurements to be made on solid polymers, which would normally be too broad to evaluate. Typical nuclei investigated are ^{13}C and ^1H , with ^{13}C providing superior resolution but ^1H requiring much shorter data acquisition times.

In addition to analytical improvements allowing for observations of nuclei and their chemical environments in the solid state by MAS, the physics of nuclear spin and diffusion within an NMR magnetic field has allowed accurate measurement of specific motions and characteristic times of those motions in the solid state. Thus, examples of critical information that can be provided by solid-state NMR are:

- (i) Spatial order and connectivity
- (ii) Small-molecule interactions
- (iii) Surface interactions
- (iv) Polymer dynamics and their temperature dependence
- (v) Reaction monitoring
- (vi) Site activity
- (vii) Blend miscibility

Limitations of solid-state NMR are:

- (i) Time intensive
- (ii) Cost
- (iii) Low sensitivity for some nuclei

Since polyurethanes are often multiphasic materials consisting of low glass transition temperature soft segments cross-linked by high glass transition hard segments, the opportunity for developing quantitative understanding of these motions and the resulting polymer properties is apparent. The use of specified pulse sequences such as Hahn spin-echo techniques allows correlation of NMR-determined spin-oriented relaxation times with morphology and mobility [97–99]. Specific to polyurethanes, the mobile soft segments and the rigid hard domains should represent clearly distinguishable environments with substantially different relaxation times. In fact, it is observed that the spin–spin relaxation time (the product of a spin-echo experiment, distinct from a spin–lattice relaxation) for hard segments is 7–20 μs , while for soft segments it is 200–1000 μs [100]. As a matter of practicality, proton relaxation

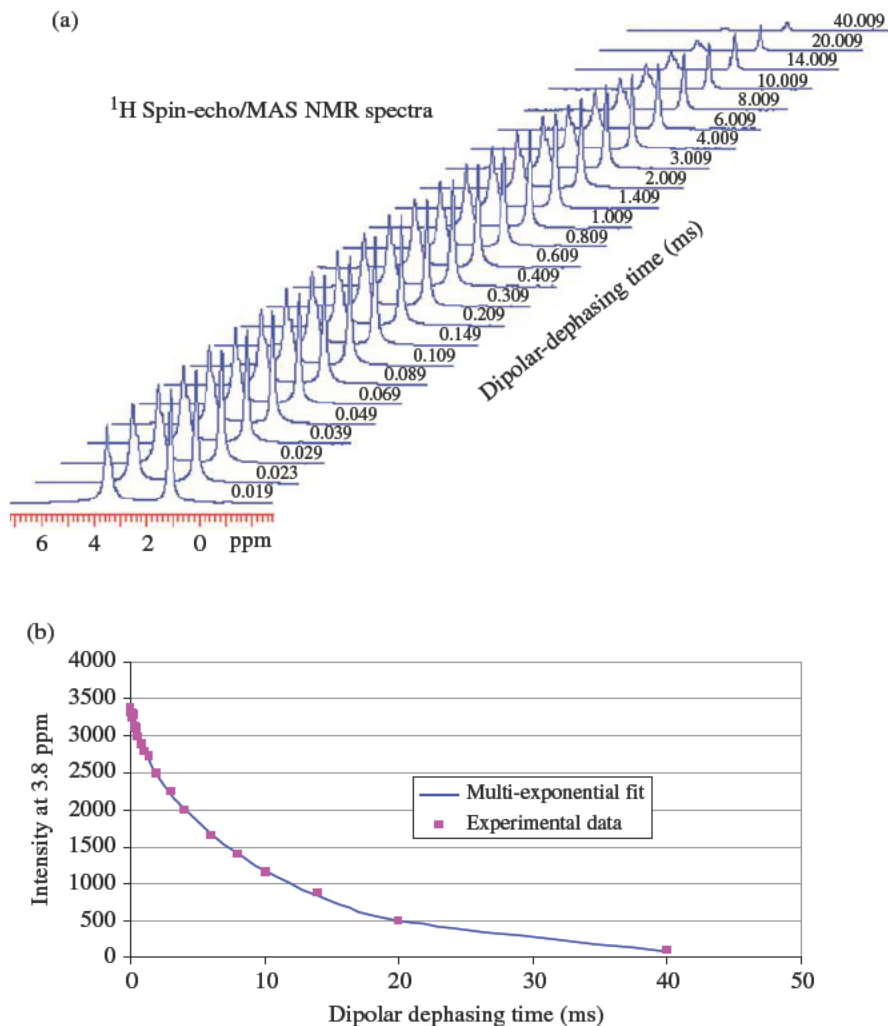


FIGURE 5.29 (a) Representative stack plot of ^1H MAS NMR spectra of a polyurethane foam acquired at 38°C with values of the ^1H dipolar dephasing time indicated using the Hahn spin-echo technique. The resonance at 3.8 ppm reflects components of propylene oxide and ethylene oxide from the soft segment backbone, while the resonance at ~ 1 ppm is from the pendant methyl unit of propylene oxide. (b) Representative biexponential fit to data obtained from stack plot data. Reprinted with permission from Ref. [16]. © Elsevier Pub.

spectra are usually obtained for soft segment dynamics due to their higher mobility and accompanying longer dipolar dephasing time constants. Hard segment dynamics will often be probed by ^{13}C NMR due to greater difficulty in resolving individual hard segment ^1H peaks appearing often as a broad peak with spinning side bands extending over a wide frequency range [101].

The different scale of hard and soft segment relaxation times in the spin-echo experiment allows for isolation of the two phases and analysis of each phase for its particular characteristics [102]. In the event of each phase existing in a homogeneous environment, the relaxation decay will appear as a single exponential decay. In the event that a single phase comprises more than one environment, each environment results in a distinctive spin–spin relaxation time, and the relaxation may be well fit to a multiexponential decay described by Equation 5.15:

$$M(t) = M_o \sum_i P_i e^{-t/T_{di}} \quad (5.15)$$

where P_i and T_{di} are the percentage and dipolar dephasing time constants for the i th component, respectively [103].

An example of experimental data and analysis is shown in Figure 5.29. A time-resolved stack plot of ^1H MAS NMR spectra of selected resonances of a polyurethane soft segment is shown with the dipolar dephasing time indicated using the spin-echo technique. The least squares analysis of intensity for a specific resonance versus dipolar dephasing time provides the best fit for the dipolar time constants, which can then be interpreted to infer the mobility of a percentage of soft segment components and their subsequent role in measured polyurethane properties [16]. In the particular case of Figure 5.29, the multiexponential fit is well characterized by two time constants: one fast and one much slower. An interpretation of this observation might be that a percentage of the soft segment is mobile reflecting dynamics typical of an unencumbered soft segment, while another component is highly reflective of hard segment dynamics due to dipolar and hydrogen bonding at the hard segment–soft segment boundary. The temperature dependence of the component percentage and time constants can provide additional insight into the molecular-level dynamics responsible for observed polymer properties.

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6

POLYURETHANE FLEXIBLE FOAMS: CHEMISTRY AND FABRICATION

Flexible polyurethane foam is the largest volume application for polyurethanes and the largest category of cellular polymeric materials [1]. The discussions in prior chapters relating to foam properties and chemistry apply to flexible foams from a fundamental standpoint. Polyurethane chemistry is flexible enough and can incorporate enough components that the potential variability in chemistry and process makes drawing hard rules about foam formulation a fruitless task. In fact, the properties of a particular foam can often be achieved by numerous combinations of foam components. Despite this challenge, it is still possible to generally discuss concepts and guidelines for foam production and methods of making foams at various scales. Furthermore, even though there are many ways to make foam, there are many fewer ways to describe the product, its performance, and the physical paths that the reactants take to the final product. This chapter will broadly define design concepts for making polyurethane flexible foams, physical concepts relevant to the formation of foam from polyurethane components, and physical descriptors of the product. Discussion of the building blocks can be found in Chapter 2, the chemical reactions that occur during foaming in Chapter 3, theoretical concepts in polymer formation and foam structure in Chapter 4, and analysis of polyurethane foams in Chapter 5.

6.1 MAKING POLYURETHANE FOAMS

Industrial production of foams is a highly optimized and reproducible operation. The volumes of chemicals consumed in a commercial-scale plant can be startlingly large, and a large plant operating at capacity can be a supply chain challenge. The production of foam after receipt of raw materials subsequently becomes an exercise in accurate mixing and pouring. The necessary requirement is to perform these mixing operations in the right amounts, in the right order, and at the right time. When done correctly, the physical processes that result in foam can be relied upon and reproduced such that a stopwatch may not detect variability between repetitions. Thus, the first step to making a foam is to assemble all the necessary reagents in sufficient amounts and accurately dispense them into a reaction volume.

When making flexible foam, calculation of the correct mass to mix of a particular ingredient is normally based on the *equivalent* weight of the component rather than the molecular weight of the component [2]. The equivalent weight is simply the molecular weight of the component divided by its functionality. In setting formulation, the stoichiometry is set to match the equivalence of the isocyanate side with the total equivalence of the isocyanate-reactive side because the materials to be mixed may have quite different functionalities, but controlling stoichiometry is a necessary condition of getting a good result. The use of equivalence minimizes the likelihood of stoichiometry errors, though they do still occur.

As mentioned earlier, there are many desired flexible foam applications and a defined recipe for making each one. Flexible foams can be produced for applications such as mattresses that may be cut from large blocks into defined shapes for the application. These foams are often called *slabstock foams* since the foams are made as enormous slabs from which the desired product is cut. Alternatively, the foam can be poured into a predefined mold to form a custom shape. Such foams are often found in furniture cushions and automotive seating and for obvious reasons commonly called *molded foams*. The distinctions between slabstock and molded foams form a large enough class boundary that their formulations can be distinguished by basic rules.

6.1.1 Slabstock Foams

Slabstock foams, like most foams, are prepared from polyols, isocyanates, and water. Along with these basic ingredients are added catalysts, surfactants, coblowing agents, flame retardants, antioxidants, and sometimes colorants. All of the nonisocyanate components are premixed in combinations that are convenient for the foam manufacturer and then vigorously mixed with the isocyanates. The mixed and reacting system is applied to a moving belt (Fig. 6.1). The large foam slab (sometimes also referred to as a “bun”) is subsequently cut into manageable sizes, set aside in a well-ventilated location to cool and complete its cure. The actual geometry of a particular slab foam production line may vary from that diagrammed in Figure 6.1 but will in essential details be similar. The ventilation requirements are due to the substantial exotherm from heat of reaction and the volatility of the polyurethane components, particularly isocyanates, catalytic amines, and small-molecule impurities from the polyol production—mostly aldehydes. Control of the exotherm is

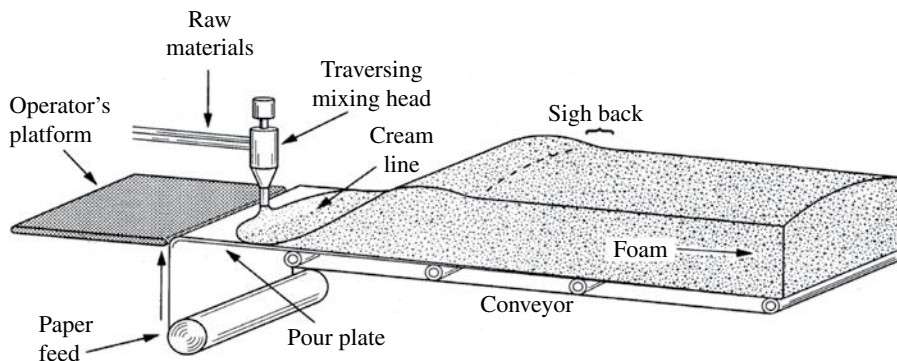


FIGURE 6.1 Slab foam process. The image does not show the feed tanks, ventilation, or substantial amount of electronic controls involved. Reprinted with permission from Ref. [3]. © John Wiley & Sons, Inc.

critical to prevent oxidative discoloration of the foam center referred to as “scorch.” In the extreme, a foam may even catch fire if the foam interior temperatures are not controlled.

Typical foam formulations that could be attempted by an experimentalist with a high probability of success would be exemplified by those found in Table 6.1. These two recipes are distinguished by the amount of water and the amount of isocyanate, in this case toluene diisocyanate (TDI). The effect of increased water and concomitant TDI is to (i) reduce the foam density with higher water (increase the amount of bubble formation due to the isocyanate–water reaction that produces CO_2 (Chapter 3), (ii) increase the foam stiffness due to additional urea formation that further reinforces the foam with a high modulus block (Chapter 4), and (iii) increase the exotherm produced by the foam as it rises.

TABLE 6.1 Representative slab foam recipes. To make these foams in a lab, place all components in a well-ventilated fume hood with an accurate scale. Mix all but the isocyanates in a beaker. Add isocyanate to beaker, mix vigorously for 10 S, and pour into a box adequate for the volume expansion. Clean removal of the foam from the box will probably require the use of a release paper liner. Perform in a well-operating chemical hood with appropriate personal protections

Component	Functionality	Molecular weight	Equivalent weight	Formulation 1	Formulation 2
				grams	grams
Polyol	3	3000	1000	100	100
Water	2	18	9	2	4
TDI (at 110 index)	2	174	87	30.6	52.1
Surfactant DC5125				1	1
Triethylenediamine				1	1
Tin dioctanoate				0.15	0.15

The stoichiometry of the reactive components is matched so that the total equivalents of isocyanate and isocyanate-reactive components are matched. There is a 10% excess equivalence of TDI added in this case (110% of equivalence referred to as “index”). This is done to assure that all of the active hydrogen components are tied up to make a complete network. Some of the excess isocyanate is volatilized as previously mentioned. Some of the excess is employed to cover any loss of isocyanate functionality due to dimer formation, unintentional urea formation due to reaction with adventitious water, and cross-linking isocyanate–isocyanate reactions due to excess concentration fluctuations (Chapter 3). Formulations of Table 6.1 can be scaled up by proportionality, but the experimentalist should always be cautious due to the increasing adiabatic heating of the foam and its high insulation properties.

The quantification of hard segment in the foams of Table 6.1 can be described by either the percent hard segment or the hard segment length. The percent hard segment is simply the sum of grams of water and isocyanate divided by the total mass of the foam. The length of the hard segment can be calculated from the sum of molecular lengths making up the hard segment times the average hard segment oligomer number. Alternatively, it can be easier to simply refer to the hard segment length based on the average number of urea repeat units between polyol soft segments easily approximated by the equivalents of water divided by the equivalents of polyol in the formulation [4]. Table 6.2 provides an illustration of this variation for the foam recipes of Table 6.1. It is clear that there are no fractional hard segment lengths such as 2.2 or 4.4. This number merely indicates that most hard segment lengths will be about 2 or 4. As discussed in Chapter 5, one can expect that there will be a significant amount of isocyanate that is reacted with only polyol and there will be hard segment blocks with a significantly larger number of repeat units greater than 2 or 4, but these will average out to approximately 2.2 or 4.4.

The properties of the two foams defined in Tables 6.1 and 6.2 will be primarily determined in these particular cases by their density and the percent hard segment. On reflection, it is apparent that these two quantities are not independent of each

TABLE 6.2 Alternative methods of describing the hard segment content of a polyurethane foam

Recipe	Grams H ₂ O	Grams polyol	% hard segment	$\frac{[\text{equivalents H}_2\text{O}]}{[\text{equivalents polyol}]}$
1	2	100	24.6	2.2
2	4	100	35.9	4.4

TABLE 6.3 Property range of a conventional slabstock foam made from the recipes of Table 6.1

Property	Recipe 1	Recipe 2
Density (lbs/ft ³)	2.4–2.8	1.6–1.9
Tensile strength (lbs/in ²)	20–24	18–22
Tensile elongation (%)	180–230	170–210
Airflow ft ³ /min	2–4	3–5

other since more water increases percentage hard segment and reduces foam density as more CO₂ and heat are generated. The increasing temperature and gas pressure creates expansion pressure on the growing foam and so reduces density. However, while additional water creates additional hard segment and stiffening of the foam, a higher foam density obtained by reducing water will also make for harder foam by virtue of more massive struts making up the foam structure [5]. A range of selected properties that might be obtained from foam recipes 1 and 2 are given in Table 6.3.

High-resilience (“HR”) slabstock foams are made by a similar process to the conventional slabstock foams described earlier, but there are substantial formulation and performance differences. The HR designation reflects the increased elasticity of these foams as measured by a ball rebound test (Section 5.3.1, ASTM test D2632 [6] replacing D3770). A standardized steel ball is dropped from a prescribed height and the rebounded height measured. A typical conventional foam may have a rebound resilience of 40–50%, while HR foams will usually be greater than 55%. HR foams are also referred to as “comfort” foams due to this enhanced energy return upon compression. The uses of HR foams are typically as higher-quality mattresses and furniture cushions. From the formulation standpoint, the biggest difference is the polyol structure. As shown in Table 6.1, conventional slabstock foams typically have hydroxyl equivalent weight on the order of 1000 g/eq and are triols made entirely from propylene oxide (PO). All PO polyols have only secondary hydroxyls to react with isocyanates. In contrast, HR slabstock foam employs polyols with functionality of three or greater and hydroxyl equivalent weight of between 1500 and 2000 g/eq. Since higher equivalent weight polyols have less functionality to react with isocyanate per unit mass, they are intrinsically less reactive than lower equivalent weight polyols of the same structure. To achieve similar reaction kinetics to conventional slabstock polyols, PO polyols are tipped with ethylene oxide (EO) to make triblock EO–PO–EO polyols having a significant amount of primary hydroxyl functionality. Primary hydroxyls are about a

factor of 3 more reactive than secondary hydroxyls and are part of the design options for optimizing foam rise and cure to meet a manufacturer’s specifications. Despite the presence of primary hydroxyls, HR foam may still collapse if there is insufficient molecular weight build to prevent foam cell coalescence. In this case, a cross-linker like diethanolamine (DEOA—Fig. 6.2) may be incorporated into the formulation [7]. DEOA has a secondary amine and two primary hydroxyls creating a low-molecular-weight cross-linking agent for isocyanates and a means of rapidly building molecular weight. DEOA not only builds foam stability as a cross-linking agent, but it can also have a significant negative effect on the ability of foam cells to rupture and reticulate throughout the foam body. The effect will be to reduce the foam’s airflow and increase foam stiffness due to hydraulic resistance to compression. This source of foam load bearing is not usually desirable since it is an artifact of processing and will change with use and age. For this reason, while DEOA is a very common constituent of foam formulations, it is used in small amounts, usually comprising less than 1% of the total isocyanate-reactive composition. Similarly, a silicone surfactant that does less to stabilize the cell wall will usually be added (medium to low efficiency) to facilitate cell window drainage to the cell interstitial boundaries (see Section 6.2.1.2).

While hydraulic resistance to foam compression is usually avoided, formulators often utilize copolymer polyols to increases foam stiffness and load bearing in HR foam (Section 2.1.4). A representative HR foam formulation and properties are provided in Table 6.4.

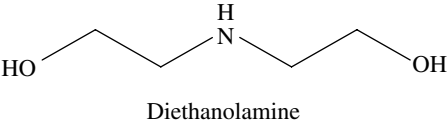


FIGURE 6.2 The structure of the common polyurethane foam cross-linking agent diethanolamine (DEOA).

TABLE 6.4 HR foam formulation and representative properties

Component	Mass
15% SAN 1870 equivalent weight 1870	100
Water	2.2
DEOA	0.7
Triethylenediamine (catalyst)	0.36
Dibutyltin(IV) dilaurate	0.25
Medium-efficiency silicone surfactant	1
TDI (115 Index)	31.8
Density (lbs/ft ³)	2.6
Tensile strength (lbs/in ²)	17
Elongation at break (%)	150
Resilience (%)	60
Tear strength (lbs/in ²)	1.4
90% compression set (%)	5

6.1.2 Molded Foams

Preparation of molded foams is a widely practiced technology, and the varieties of molded foam formulations are at least as varied as those for slabstock. The concept of molded foam production is simple: the components of the foam are mixed and injected or poured into a premade mold that the foam fills as it forms. The foam has a set residence time and is removed after a designed-for residence time in the mold. After removal from the mold, the foam is set aside to finish curing. As practiced industrially, molded foam technology is highly optimized from the point of view of reproducibility of processing and properties. In contrast to slab foam production, in which parts must be cut from a block, molded foams produce the final part as part of the foaming operation. While this aspect reduces scrap rates and removes the cutting operation of making a finished part, the mass throughput of a molded foam plant is lower and requires the presence of molds, which can be quite expensive. In typical molded foam operations, molds are placed on carousel or oval racetrack fixtures that rotate such that the timing of foam residence is matched to the time it takes for the carousel to make a cycle and the mold be refilled.

Besides the operational details, manufacturers choose to make molded foams because of the intricate shapes they are trying to fabricate and the ability to overmold specific objects within the shape such as functional parts, decorative skins, or reinforcements. The structure is engineered to provide the correct appearance, function, and shape as a composite part.

Figure 6.3 shows the components of a molded foam production in terms of handling of raw materials and then mold filling. The isocyanate-reactive parts (polyols, chain extenders, surfactants, catalysts, water, etc.) are put into their joint tank or individual tanks and then mixed with the isocyanate in a high-energy mixing head. The mixed components are injected into the mold, the mold closed, and the components allowed to cure.

Because of the need to optimize efficiency of molded foam manufacturing and at the same time produce foams of exceptional durability, comfort, and variety, the formulation of molded foams is complex and could be described to some extent as an art. The speed of the molding, pouring/injecting, and curing process is all controlled by the chosen foam formulation. Similarly, details of the manufacturing operation can have a significant influence on formulation design. For instance, if the foam molds are heated, then a less reactive system can be employed, and if the molds are unheated or heated to a lower temperature, then another formulation will be chosen. In some cases, the mold is partially filled with a polyurethane formulation to produce a specific characteristic and then filled subsequently with another formulation to produce desired characteristics for the rest of the part. This flexibility of molded foam operations makes it very desirable for specialty part production but also contributes greatly to the complexity of the formulation science.

As previously mentioned, examples of molded foam formulations are bound to be inadequate in reflecting the range of available options. However, the basic categories of components used in molded foams are similar to those used for HR slabstock foams. If the manufacturer is actively heating his/her mold, by passing through a

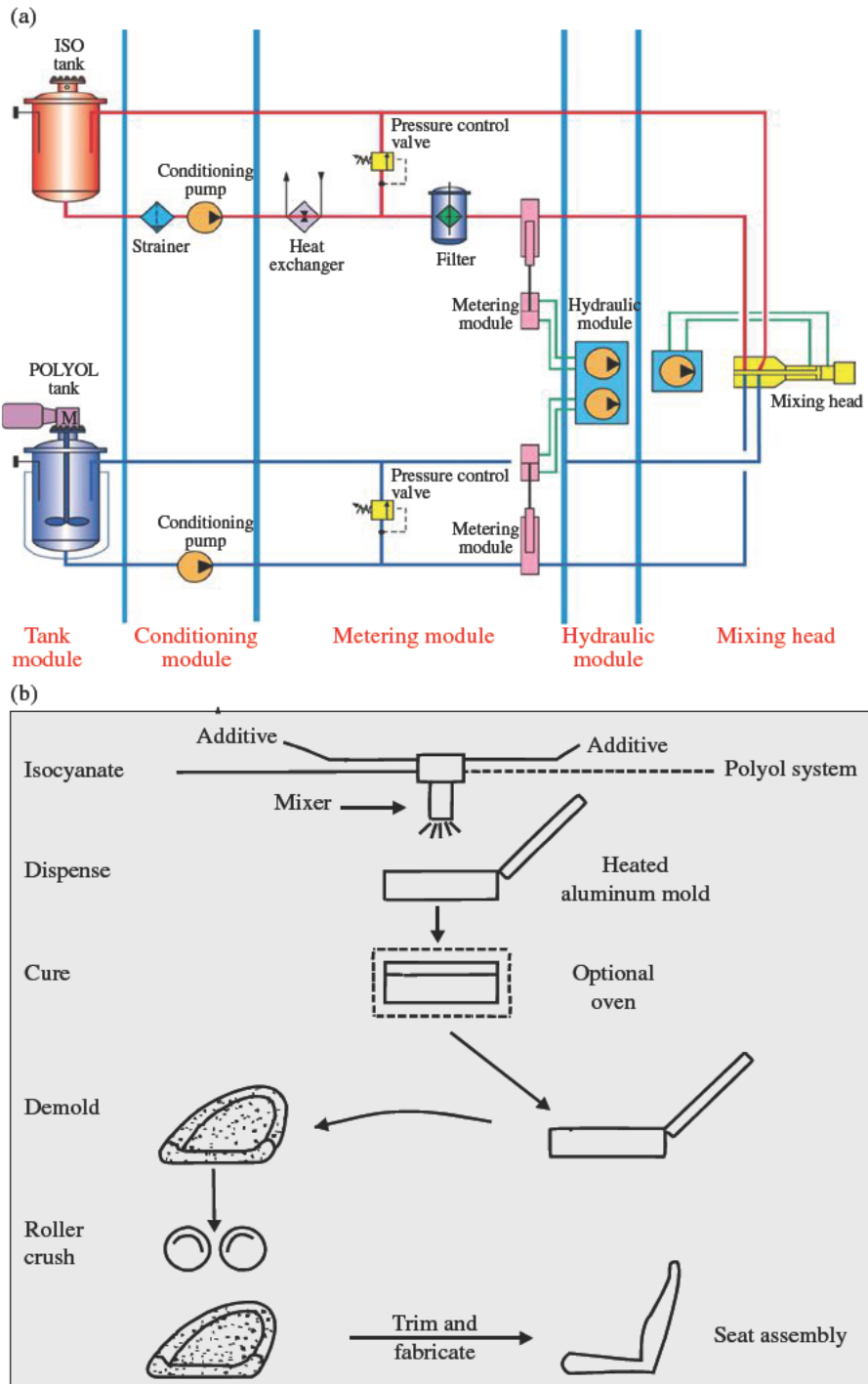


FIGURE 6.3 Molded foam operations. (a) Raw material handling and (b) foam fabrication. Reprinted with permission from Ref. [3]. © John Wiley & Sons, Inc.

hot oven, for instance, this will be termed a “hot cure” molded foam. In this case, the formulation will employ polyols that may be 3000 molecular weight triols (1000 g/eq OH) that will be a triblock of PO capped by EO tips. The polyol will be approximately 20% by weight EO (more by molarity) to assure that the great majority of end groups will be faster-reacting primary hydroxyls. A manufacturer may use TDI, blends of TDI with polymeric MDI (pMDI), or pMDI. The choice is dependent on price, preference of the manufacturer, and in some cases geography where a particular isocyanate may be preferred based on convention. Table 6.5 offers examples of hot molded foam formulations to make foams of differing hardness. The formulation shows the role of copolymer polyol in hardening foam even in the case of lower overall hard segment. Of course, the reduced overall mass of hard segment is crowded into a smaller volume as well since the hard segment is excluded from the space occupied by the SAN particles.

HR molded foams are also sometimes referred to as “cold cure” HR foam in distinction to the “hot cure” foams described earlier. They are a more recent industrial innovation relative to hot cure foams and are differentiated by cooler mold and cure oven temperatures. These foams usually offer resiliency greater than 60%, and as high as 70% has been reported [8].

As with HR slabstock foams, HR molded foams utilize higher-molecular-weight polyols, typically 4000–6000 triols with relatively high amounts of EO capping (up to 85% primary hydroxyl functionality at 25% EO incorporation) to increase reactivity [9]. The higher reactivity of EO-capped polyols allows the formulator to use less gelation catalyst but can dictate the intensified use of blowing catalyst to make sure that the urea hard segment forms in kinetic equilibrium with the urethane reaction that builds molecular weight. Lower temperatures and retarded blow conditions often result in HR molded foams having a larger than desired population of foam cells with intact windows. It is often protocol in manufacturing to mechanically crush the foam after retrieval from the mold in order to break open cells and so increase airflow and foam breathability. While it is in principle possible to formulate so that the crushing operation is superfluous, insuring completion of the gelation

TABLE 6.5 Representative formulations for making “hot mold foam” of two hardnesses

Component	Soft foam	Harder foam
3000 molecular weight triol 25% EO	80	
1300 equivalent weight 26% solid SAN copolymer polyol	20	100
High-efficiency silicone surfactant	1	
Medium-efficiency silicone surfactant		0.8
Bis(dimethylaminoethyl)ether (blowing catalyst)	0.1	0.05
Triethylenediamine (strong gel catalyst)		0.1
N,-dimethylaminoethyl morpholine (less strong gel catalyst)	0.4	
Tin dioctanoate	0.05	0.1
water	2.4	2.1
TDI (100 index)	30.9	27

reaction so the foam doesn’t collapse supersedes the nuisance of the mechanical manipulation of the foam to maximize openness. These are the kinds of considerations of practical foam formulation. An example of a TDI HR molded foam formulation is provided in Table 6.6.

A common variation of the formulation of Table 6.6 is to substitute a blend of TDI and pMDI to provide foam properties intermediate between the foams produced by either isocyanate on its own. An example of such a formulation is provided in Table 6.7.

Some molded foam producers manufacture only with pMDI as the isocyanate. The choice is largely a matter of preference including the better health and safety profile of pMDI due to its lower volatility; however, there are several differences in foam properties between foams made with TDI and pMDI. One difference is that pMDI foams generally cure faster due to the uniform reactivity of MDI isocyanate functionality (the second isocyanate reaction on TDI is usually significantly slower than the first). While speed is a preferred attribute in molded foam operations, rapid viscosity increase can interfere with complete mold filling. However, when formulated effectively, pMDI foams can be made with shorter cycle times. This attribute can also allow the manufacturer to lower their mold and oven temperatures to further balance chemical and process kinetics. The larger molecular volume of pMDI relative to TDI also means that the volume of hard segment produced for an MDI foam is higher than that for a TDI foam. This different molecular volume results in MDI-

TABLE 6.6 Representative formulation for a high-resilience “cold mold foam”

Component	Parts by weight
40% SAN EO-capped PO triol of ~1800 g/eq OH polyol	70
40% solids EO-capped PO triol ~2350 g/eq OH polyol	30
Diethanolamine (cross-linker to speed up gelation)	1.25
Triethylenediamine (gel catalyst)	0.25
Bis(dimethylaminoethyl)ether (blow catalyst)	0.1
Silicone surfactant for HR foam	1.0
Water	4.0
TDI (100 index)	43

TABLE 6.7 Representative formulation for a high-resilience “cold mold foam” using blended isocyanates

Component	Parts by weight
40% SAN EO-capped PO triol of ~1800 g/eq OH polyol	70
40% solids EO-capped PO triol ~2350 g/eq OH polyol	30
Silicone surfactant for HR foam	0.7
Triethylenediamine	0.3
Bis(dimethylaminoethyl)ether (blow catalyst)	0.1
Water	3.5
80% TDI 20% pMDI with 136 g/eq isocyanate (100 index)	42.7

TABLE 6.8 Representative formulation for a high-resilience “cold mold foam” Using PMDI

Component	Parts by weight
14% EO-capped 1600 equivalent weight PO triol	98
74% EO-capped 1700 equivalent weight PO triol for enhanced cell opening	2
Silicone surfactant	1
Diethanolamine	0.5
Triethylenediamine	0.5
Bis(dimethylaminoethyl)ether (blow catalyst)	0.1
Water	3.4
pMDI prepolymer 18.7% isocyanate (100 index)	99.5

based foams having potentially higher load bearing at a given water and isocyanate index than TDI. It has been noted however that higher-index molded foams may exhibit degradation in some dynamic properties while exhibiting higher hardness. A representative formulation is provided in Table 6.8.

A complicating aspect of foam formulation alluded to earlier is the conventional aspects of molded foam usage. This is greatly influenced by regional perceptions of comfort that is then related to the foam stiffness, resilience, and breathability (related to airflow). Another foam feature dictated by regional preference is the rate of change of resistance with increasing compression (sometimes called the “support” or “comfort” factor and defined quantitatively by the ratio of foam stiffness at two different compressions) [10]. Foam formulation factors that the foam designer may vary to meet these customer preferences are:

- Foam density (influenced by water level and percentage hard segment)
- Cell structure and foam openness (dictated in part by surfactancy and catalysis)
- Isocyanate type and index
- Polyol functionality and equivalent weight
- Copolymer polyol and percentage solids
- Additives, inserts, and seat design

6.2 FOAM PROCESSES

While it is a nearly hopeless task to provide specific guidance for making foams due to the huge number of possible components and desired properties, it is possible to understand the basis for the foam formulator or designer to choose components. Regardless of the foam production format (i.e., slabstock or molded), the same physical processes occur, and the timing and intensity of the chemical reactions while the foam is forming must be controlled. Figure 6.4 shows a timeline for the various individual processes that the choice of components, catalysis, surfactancy, temperature, and myriad process details can affect.

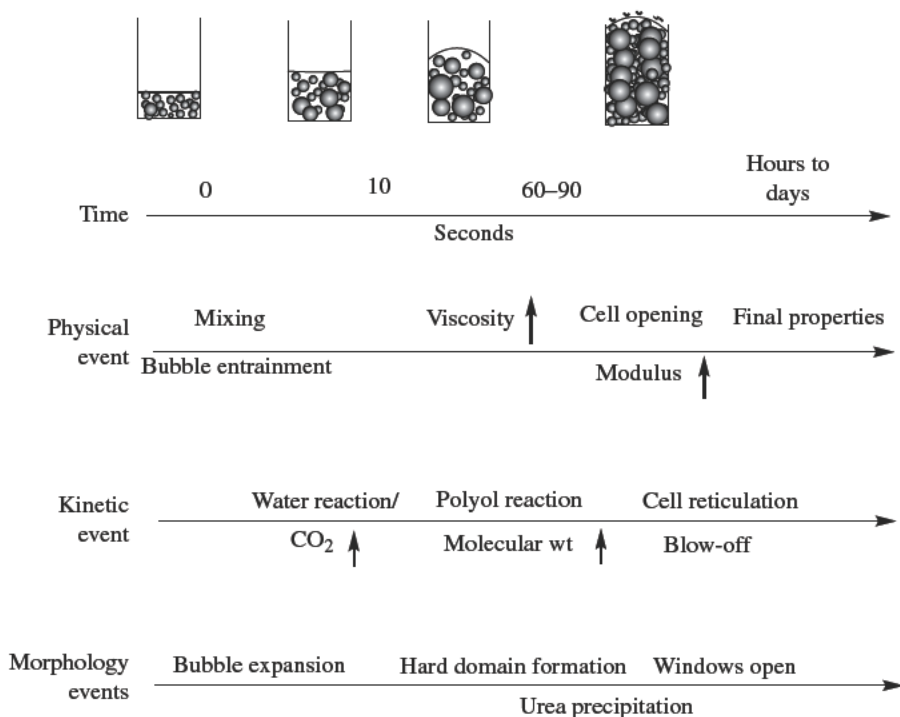


FIGURE 6.4 Timeline for the physical and chemical processes occurring in polyurethane foaming. Reprinted with permission from Ref. [3]. © John Wiley & Sons, Inc.

Along the timeline, individual processes can be codependent (for instance, bubble entainment, CO₂ generation, and bubble expansion), can be competitive (for instance, the water reaction vs. the polyol reaction with isocyanate), and can be consistently coincidental, but with no clear connection (for instance, urea precipitation with cell opening) [11].

As indicated in Figure 6.4, the first process is mixing, which involves bubble entainment. Surprisingly, this is a critical aspect of the foaming process since it has been shown that no new bubbles are formed after this step, and all subsequent processes are bubble growth and coalescence [12]. Thus, the work put into this step by mixing is a critical aspect, and mixer technology is a proprietary and protected intellectual asset. While CO₂ produced by the isocyanate–water reaction can in principle nucleate and form a bubble that can expand, this is in fact a highly unlikely event. The reason is because the bubble nucleus will of necessity be very small and the increase of free energy (ΔF) to form the bubble has the following relationship to the radius of the bubble (Eq. 6.1):

$$\Delta F > \frac{3\gamma}{r\rho} \quad (6.1)$$

where γ is the interfacial surface tension, ρ is the gas density, and r is the bubble radius. The very small size of a nucleating bubble insures that the energy input to form those bubbles spontaneously will be immense [13, 14]. Video recording experiments have been performed, which seem to confirm that no new bubbles are formed in the foaming process after mixing. CO_2 produced from the isocyanate–water reaction diffuses to the already existing bubbles and solely affects the growth of those bubbles. Reacting polyurethanes that do not have bubbles produced by the mixing process are not observed to foam in any substantial way [15–17].

Following the timeline of Figure 6.4, with the initial rush of bubble expansion (and the increasing system temperature associated with the water–isocyanate reaction), the polyol–isocyanate reaction accelerates, and the system viscosity increases due to increasing molecular weight. With increasing viscosity, the system develops a viscoelastic response to the upward pressure of the expanding gas bubbles. As the gas bubbles contact each other, their initial contact points preferentially increase in size transforming the spherical bubbles into polyhedra. If unimpeded, the gas bubbles grow, coalesce, and burst prior to the system developing sufficient elasticity to stabilize the foam structure. If viscosity increases too quickly such that the cell windows cannot thin and retract to the plateau borders (Fig. 6.5a), the cell windows will remain in place resulting in closed-cell or partially closed-cell foam (Fig. 6.5b). Flexible foams with a large number of unruptured cell walls will present a hydraulic resistance to foam compression (see Section 4.2.2.2 for a quantitative treatment), resulting in the foam being termed “tight.”

As discussed in Chapter 4, at some time, the polyurea hard segment will phase separate from the chain extending soft segment to assemble into a microphase structure dependent on the phase incompatibility (quantified by the Flory χ value) and the molecular weight of the phase. This precipitation event is often witnessed to occur just prior to the simultaneous cell wall breakages and foam reticulation into an open-cell foam. The reticulation event can in some cases be observed as an effervescence of gas off the top of the foam bun (termed “blowoff”). The coincidence of these events has led some researchers to speculate that the precipitation is itself the determining event for the timing of foam reticulation. However, arguments have been made that the timing of the events is coincidental and not physically dependent [11].

A method of visualizing and timing the events of polyurethane foaming is to perform an experiment as shown in Figure 6.6 [3]. In this experiment, all of the isocyanate-reactive components and the catalysts are placed in one beaker and mixed with a high-shear mixer. For this experiment, no surfactant is included so that the bubbles grow but collapse rapidly resulting from rapid drainage of the polymer bubble structure. The isocyanate is then poured into the first beaker and the polyurethane formulation again mixed with high shear for a short time (ca. 10 s), and the whole formulation then poured into a disposable plastic bag as shown in Figure 6.6. Following the timeline of Figure 6.4, all of the processes are visible except the growth of the foam into a bun. The bubbles grow and escape through the top of the bubbling mixture. At some point, the polyurea hard segment exceeds its compatibility with the soft segment and precipitates as a white mass at the bottom

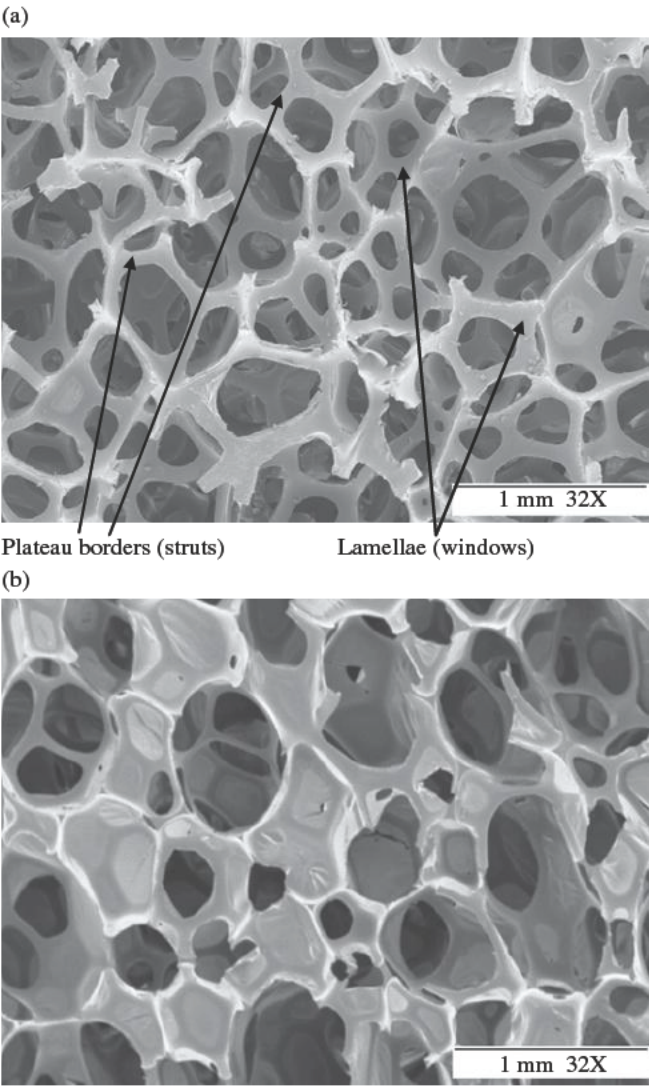


FIGURE 6.5 Scanning electron microscope images of flexible foams. (a) An open-cell foam that has had nearly complete drainage of the window materials into the bubble walls (termed the plateau borders (struts)). Remaining bubble windows are indicated. (b) A flexible foam showing the effect of kinetic imbalance such that the chemical processes were truncated before cell windows (lamellae) were drained into the plateau borders.

of the bag. When this experiment is performed carefully, the time reproducibility of the events is within 1%. This experiment is especially useful when comparing foaming kinetics with a new foam component to a well-known benchmark foam composition (Table 6.9).

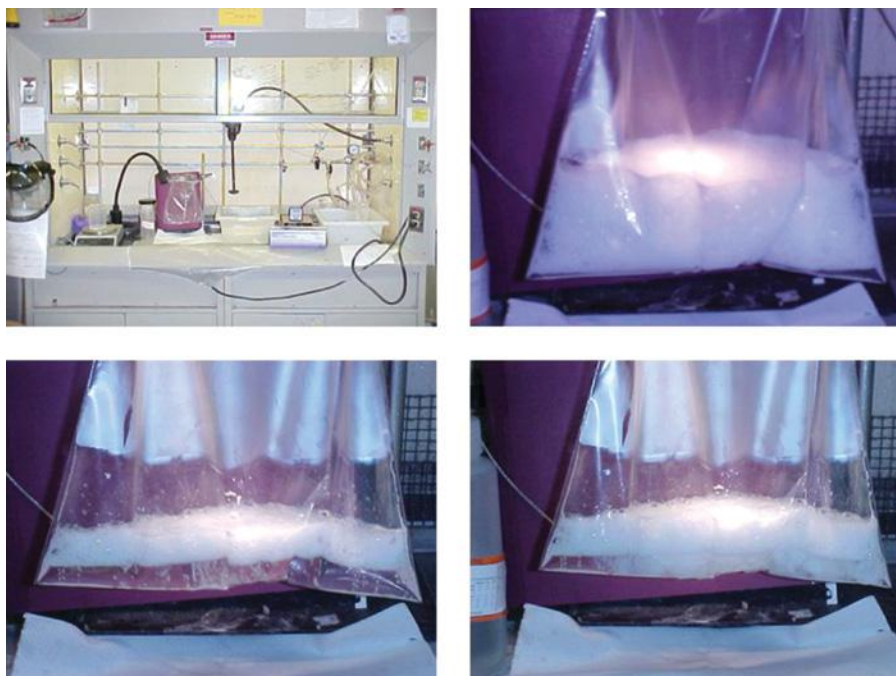


FIGURE 6.6 A useful experimental technique for evaluating the timing of urea precipitation in a foam formulation. Top left: the experiment is performed in a well-operating fume hood. Top right: after mixing of the components and dumping into the disposable plastic bag (see text), the water reaction to urea and CO_2 formation are readily visible. Bottom left: the water reaction begins to slow and the urethane reaction begins to accelerate. There hasn't been any microphase separation as observable by the lack of precipitate in the bottom clear liquid. Bottom right: urea precipitation is clearly visible marking the beginning of microphase separation. Reprinted with permission from Ref. [3]. © John Wiley & Sons, Inc.

TABLE 6.9 Effects of foam raw material structure variation on foaming and foam properties

Component	Structural variable	Effect on foaming	Effect on foam properties
Polyol	Equivalent weight	Lower—increases gelation rate	Lower—increases T_g
		Higher—decreases gelation rate	Higher—increases resilience
			Higher—increases tensile strength
Polyol	EO capping		Higher—increases d-spacing
		More—increases gelation rate	More—increases glass transition temp.
		More—increases compatibility with water	More—increases degradation of humid age properties

(Continued)

TABLE 6.9 (Continued)

Component	Structural variable	Effect on foaming	Effect on foam properties
Polyol	Functionality	More can increase gelation rate Can increase formulation viscosity More can increase foam shrinkage	Higher can increase foam hardness Less functionality can lead to less fatigue resistance Lower monol—better durability Lower monol—better dynamic properties Lower functionality—better extension properties
Water		More—increases blow reaction More—increases exotherm More—decreases shrinkage More—requires increased gel catalyst and surfactant	More—increases hardness More—increases aging degradation
Isocyanate	TDI	More—lowers viscosity Slower reacting/slower demold High NCO content	Lower-density foams Better tensile properties Not a drop-in for pMDI More stable in some molds
Isocyanate	pMDI	Faster reaction Skin formation in molds	Higher durability Harder foams
Isocyanate	Index	Higher—faster blow reaction Higher index should decrease gelation catalyst Higher—slows cure	Improved compression set Greater than 100—decreases durability Greater than 100—decreases tensile and elongation properties
Chain extender	Diol	Faster cure Faster demold	Softer foam More flexible skin (molded)
Chain extender	Diamine	Faster cure Faster demold	Harder foam Tougher skin
Cross-linker		More rapid cure Reduced flowability Faster demold	Harder foam (at density) Lower compression set Lower airflow

6.2.1 Surfactancy and Catalysis

6.2.1.1 Catalysis

The art of polyurethane foam formulation is balancing the competing processes by mixing complementary components such that all the processes of Figure 6.4 occur in amount and timing to result in foam of the correct structure and properties. Thus, along with the choice of polyol, isocyanate, amount of water, and any chain extender, the foam designer must also choose catalyst or often several catalysts and a surfactant. Once the foam designer has chosen a surfactant and suite of catalysts, the foam must then be screened by foaming at a small scale (typically 100s of grams of raw materials poured into a cardboard box with a polyethylene or Teflon film interlayer). If the choice of surfactant and catalysis is not correct, the screening foams may evidence poor foam openness (see Fig. 6.5b), shrinkage upon cooling, collapse during foaming, poor thermal properties, or even poor aging properties. If the screening foams are acceptable, there is almost invariably additional iteration when the foam is scaled to larger volumes due to the different chemical energy release and foam geometry.

The structure and mechanism of action of amine, organometallic, and trimerization catalysts are presented in detail in Chapter 3. Their incorporation into foam formulations is usually a matter of trial and error in which certain process and foam property specifications are iteratively approached. Along with the representative but far from exhaustive catalogue presented in Chapter 3, there is a growing industrial move away from utilizing organometallic catalysts and toward using reactive catalysts or autocatalytic polyols. The purpose of this industry shift is to minimize contact with fugitive heavy metals and to reduce the volatile organic components emanating from foam in day-to-day use.

Reactive catalysts are typically tertiary amines connected by a spacer group to an isocyanate-reactive group like a primary hydroxyl group [18, 19]. They are added to the formulation as one would add a conventional catalyst but typically in larger amounts. The increased usage rate is because of the lower tertiary amine equivalence per gram of catalyst and because the catalyst becomes less effective once the reactive group has been incorporated into the polymer network and is no longer able to diffuse freely. Examples of reactive catalysts are provided in Figure 6.7. Each example has isocyanate-reactive groups. The reactive group chosen for a catalyst has a significant effect on the catalyst function. For instance, a catalyst with secondary hydroxyls will react more slowly into the network than one with primary hydroxyls, so it may maintain catalytic activity for a longer period of the foaming reaction, but risks not being incorporated at all and can result in a volatile amine. A reactive catalyst with amine groups is almost certain to react into the polymer network but may rapidly lose effectiveness due to its inability to diffuse to new reactive sites. Some catalyst designs will ensure reaction into the polymer network by using a highly reactive group, but put a large spacer between the reactive group and the catalytic function that can diffuse through a relatively large spherical or conical volume even after integration into the network. These large elastically ineffective pendant groups have the potential to effect foam properties, especially aging properties.

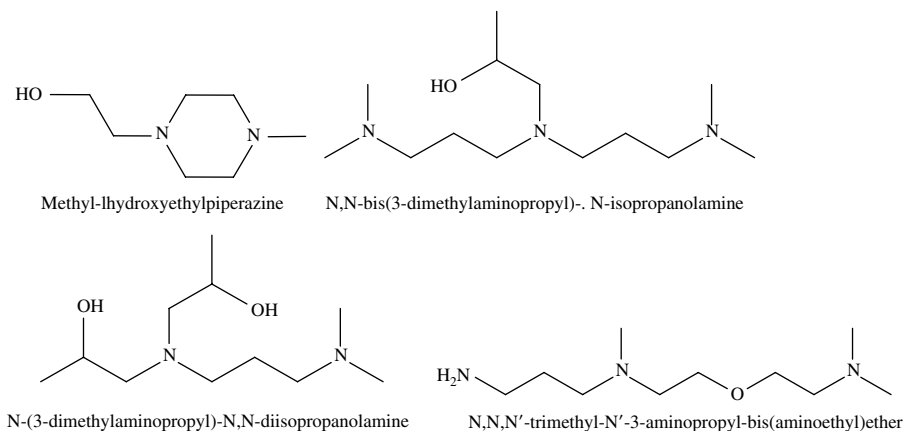


FIGURE 6.7 Examples of reactive catalyst structures. The tertiary amines are catalytic for the polyurethane reaction.

In addition to reactive catalysts, manufacturers, especially polyol manufacturers, have attempted to incorporate catalytic activity into the polyol backbone [20–22]. A relatively straightforward way is to take a reactive catalyst and grow an alkoxyate chain off of the reactive group using PO or block-polymerizing PO and EO. An example of such a procedure is shown in Figure 6.8.

The effectiveness of these reactive polyols in a foaming reaction is dictated by the same fundamental issues reflected in the behavior of any polyurethane catalyst with the additional complication of steric hindrance of alkoxyate chains and their temperature-dependent interaction with the catalytic center.

In choosing a catalyst, the foam designer must consider the characteristics of the catalyst in light of all of the processing and property attributes required by the customer. This does not always dictate the catalyst with the fastest or most balanced (blow/gelation) attributes. Table 6.10 indicates the effect of catalyst speed on the foaming process. One can see that if the preference is for a soft comfortable flexible foam, one may choose a microcellular foam with good airflow. This would dictate a certain glass transition and a certain hardness dictated by the polyol, the amount of isocyanate, and the amount of water (to control density). It might also dictate a catalyst that gels quickly to promote rapid gelation of the polymer prior to cell expansion, as well a blow catalyst that could develop sufficient pressure to burst the cells at early reaction times. If the molded foam producer needs to increase his/her throughput, he/she may want to increase his/her overall catalysis and especially his/her blow catalyst to increase the early buildup of heat, but this may dictate that the mold close much sooner than normally practiced since the foam rise may be much faster than normally accommodated.

6.2.1.2 Surfactancy

Virtually all polyurethane foams are made with the essential addition of surfactants. The role of the surfactant is still not well understood in specific detail, but a sufficient amount of controlled structure–property experimentation has been done to provide

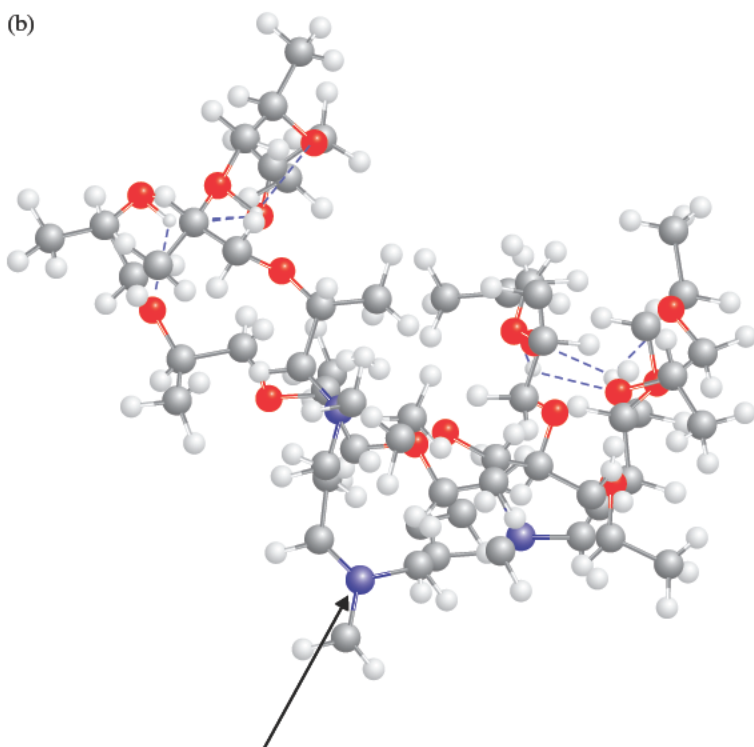
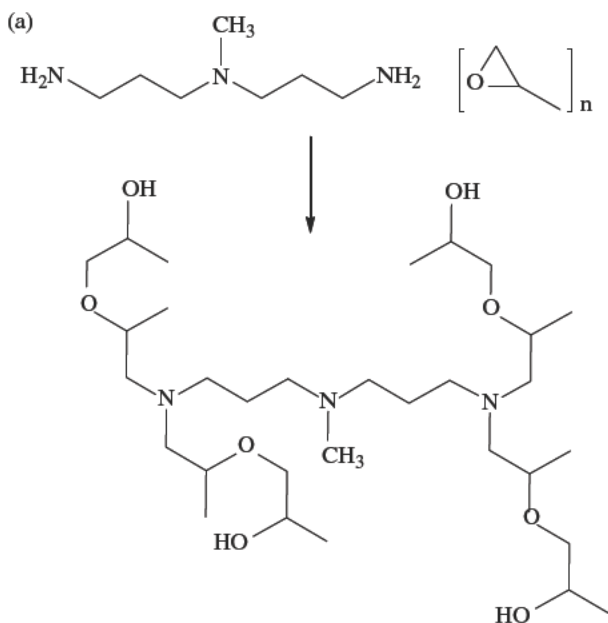


FIGURE 6.8 (a) Example reaction for making a catalytic polyol. The reaction is usually base catalyzed. (b) Energy minimized space filling structure for a reactive catalytic polyol. The arrow indicates the position of the central catalytic tertiary amines. The alkoxyated aminines are usually much less catalytic due primarily to steric hindrance as well potentially electrostatic factors associated with local ether associations. (See insert for color representation of the figure 6.8(b).)

TABLE 6.10 The effects of catalyst strength on the polyurethane foam process and foam

Activity	Effect on process and foam
Gelation	Faster gelation = Fast cure = Shorter demold times = Smaller and more closed cells = Higher density = Less flowability (faster viscosity build) = Lower airflow = More foam shrinkage during cooling
Blow reaction	Faster blow reaction = Faster creaming = Faster rise = Larger more open cells = Lower density = Lower stability (tendency to collapse) = Less shrinkage upon cooling

good understanding of desirable surfactant features for a specific foam [23]. The surfactant requirements for closed-cell rigid foam are different in detail from those of an open-cell flexible foam, but the general surfactant actions are the same.

Conventionally, it is understood that the surfactant plays no intermediary role in the reactions of isocyanates with the other foam components [24]. This is inferred by the lack of a kinetic effect in the specific reaction rate as a function of surfactant composition. However, the surfactant plays a crucial role on the foam process kinetics and eventual structure and properties. The surfactant is believed to (i) lower surface tension at the polyurethane–air interface promoting the generation of bubbles that evolve into foam cells, (ii) emulsify the incompatible polyurethane components (which does affect polymerization rate by influencing available concentration), and, most importantly, (iii) control the stability of the cell polymer surfaces. The surfaces must specialize into cell struts and windows upon packing. At a specific point of the foam rise, the cell windows must drain into the cell struts and open such that airflow through the foam is at the desired level. The details of this process are strongly dependent on the details of the surfactant structure.

The vast majority of surfactants used for making flexible polyurethane foams are of the class termed broadly as silicone surfactants. Silicone surfactants consist of polydimethylsiloxane (PDMS) backbones grafted with polyethylene oxide-co-polypropylene oxide side chains (Fig. 6.9) [25, 26].

In the early stages of foaming, the isocyanate, polyols, and water may all be mutually immiscible. The surfactant can promote initiation of the foaming reaction by specifically lowering the surface tension between the isocyanate and water phases. The structure of the silicone certainly affects this as the hydrophobic PDMS and the hydrophilic EO balance can lower the surface tension and increase the probability of reaction. As the reaction proceeds, the system advances to a single phase, and the surfactant's role as an emulsifying agent ends.

The physical mixing that occurs introduces bubbles into the reacting polyurethane components. In the absence of a surfactant or in the presence of a poorly chosen surfactant, these bubbles will coalesce, rapidly exceed the bubble wall's tensile strength,

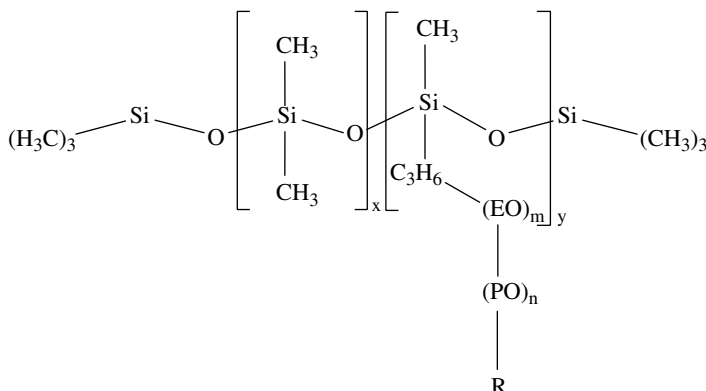


FIGURE 6.9 General structure of a silicone surfactant as might be used for polyurethane foaming.

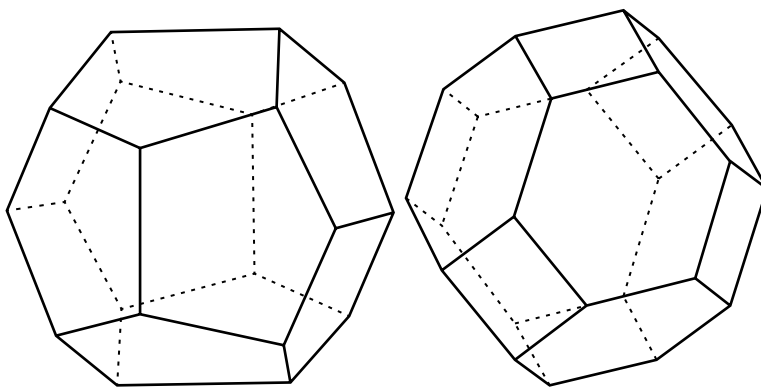


FIGURE 6.10 Suggested polyhedral structures found in polyurethane foams based on space filling considerations—left, pentagonal dodecahedron and, right, tetrakaidecahedra—compared to actual foam structures (Fig. 6.5).

and escape from the foam. If the foaming mixture has advanced its molecular weight, the reacting mixture may initially rise but will collapse. An efficient surfactant will serve to stabilize the foam structure throughout the foam process and will also control film dynamics of the growing bubbles within the foam that lead to open and reticulated cells.

In the presence of adequate surfactancy, catalysis, and a suitable mixture of polyurethane components, the foam will begin to rise. As the bubbles grow, the molecular weight of the polymer will increase providing sufficient polymer tensile properties to contain the growing internal gas pressure. When the volume fraction of bubbles exceeds 74%, the bubble growth will become limited by bubble–bubble physical interaction. The bubble will cease to be spherical and will assume a polyhedral shape as can be made out from the foam shapes of Figure 6.5. There is some controversy about the nature of the polyhedra formed (pentagonal dodecahedra or tetrakaidecahedra based on space filling surface minimization; Fig. 6.10); however, it is clear upon inspection that real foams are not regular shapes.

TABLE 6.11 Effects of silicone surfactant variables on foam process and properties

Structural feature	Effect on foaming
Polyether content	Increase in surface tension
Siloxane content	Increase—decreases surface tension Smaller bubble size
Ratio of siloxane to polyether	Increase—lowers surface tension Increase—increases bubble count Too high can be antifoaming, causing foam collapse Too low can result in too low film elasticity, causing foam collapse
Increase of molecular weight at constant siloxane/polyether	No effect on surface tension No effect on bubble count No effect on bubble size Higher film elasticity/slower drainage/more closed cells

The successful fabrication of polyurethane foam requires the *artful* balance of polymerization kinetics, competing reactions, and physical processes racing to a finished product. Small maladjustments in achieving this balance are the difference in a beautiful finished foam product and a solidified puddle of raw material. The surfactant structure–property relationships for making successful foams have been broadly defined in the literature based primarily on model compound studies. This has necessarily been the case since the vast majority of silicone surfactants are produced by manufacturers who protect structures as intellectual assets. Manufacturers instead define the surfactant in terms of efficiency in certain foam classes (i.e., slabstock, hot molded, etc.) and in terms of effectiveness at emulsification, cell size regulation, usefulness in polyester foams, copolymer polyols, specific isocyanates, and so on. Table 6.11 provides general structure–property relationships for silicone surfactants as applied to flexible foam fabrication.

6.3 FLEXIBLE FOAM FORMULATION AND STRUCTURE–PROPERTY RELATIONSHIPS

6.3.1 Screening Tests

The preparation of flexible foams will usually begin with screening of formulations. It is not uncommon for initial attempts to fail spectacularly with small foam (100 s of grams of material) made in a box rising a few inches and then collapsing. As the iterative process continues in which catalysts, surfactants, components, and their amounts are adjusted, the results will usually improve. At that point, it is necessary to obtain quantitative data on the screening studies by which to compare relatively similar results. Among the techniques are measurement of the time dependence of the foam rise and the temperature rise during the experiment. While the measurement of foam rise is relatively straightforward, the measurement of temperature requires the use of a low mass thermistor or thermocouple placed strategically in the foaming mass. The type of data obtained is typified by that shown in Figure 6.11. Within

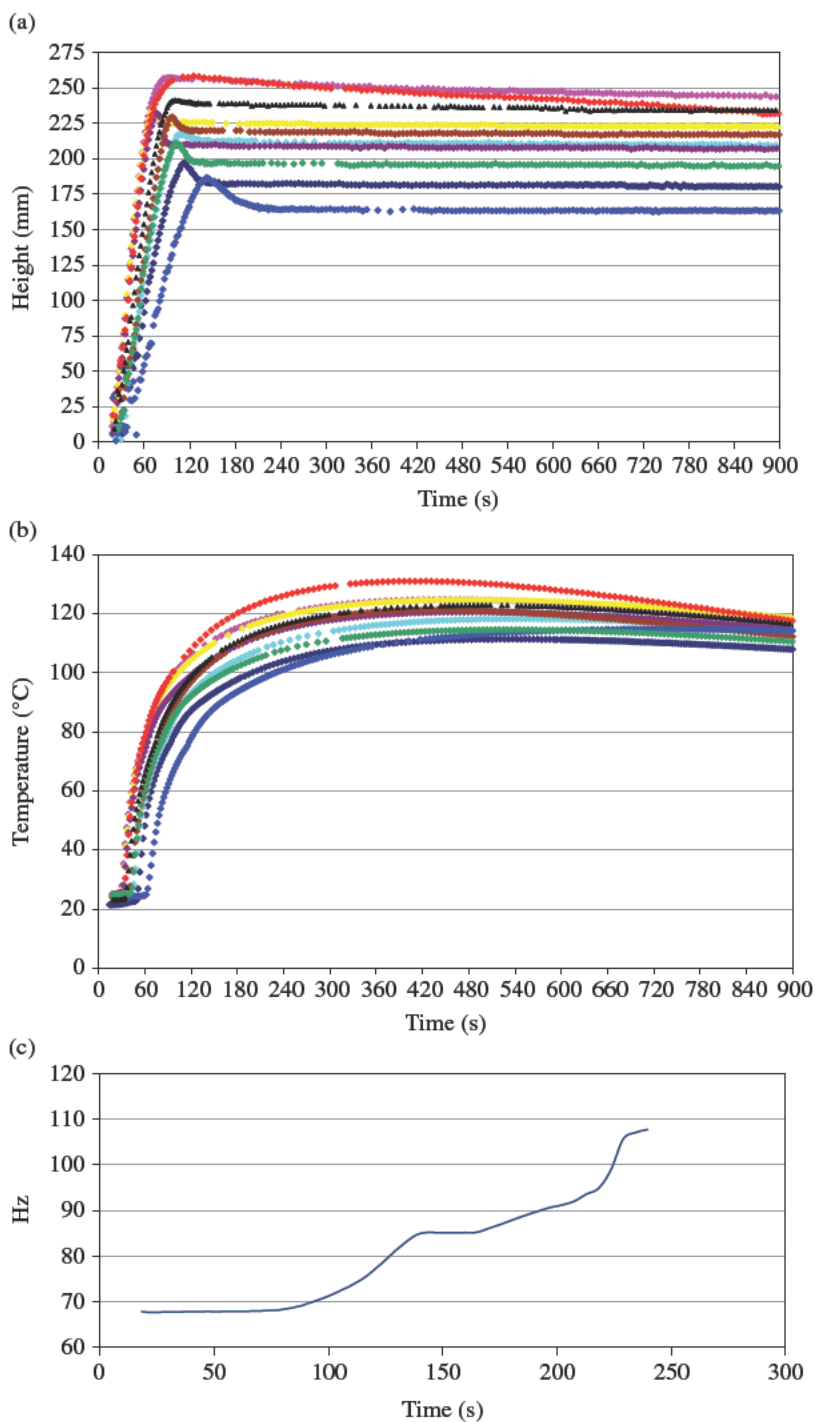


FIGURE 6.11 Measured properties from small-scale polyurethane foam screening experiments. (a) Foam height change with time. (b) Foam temperature change with time. (c) Rheology change with time—the inflection at ca. 150 s may reflect the precipitation of the hard segment. Reprinted with permission from Ref. [27]. © Elsevier Pub.

the height data, one can see that for some of the foams, there is a distinct shrinkage that occurs shortly after reaching full height. This effect is termed “sigh back” in the industry. It is a result of the loss of foam pressure holding the inflated foam coupled with insufficient polymer strength to hold the weight of the polymer. While this is not always the point of highest chemical exotherm as measured by the foam’s internal temperature, it is at elevated temperature and sets a relatively difficult to achieve criterion for the required polymer properties to maintain foam height. The temperature data is a direct measure of the rate of reaction, which is of course influenced by the formulation. It allows one to determine catalyst levels to meet the required timing of events as previously described. It is not by coincidence that in the illustrative data set, the foam exhibiting the lowest temperature, increasing at the slowest rate, also had the lowest foam rise and most severe sigh back afterward. Additionally, one can obtain a measure of the changing foam rheology with time using one of the several rheometers engineered for the purpose. These instruments typically use a vibrating probe that is submerged into the foaming mass. The change in polymer rheology affects the amount of energy needed to maintain the resonant energy or affects the frequency itself [28]. This is a notoriously tricky measurement, and the experimentalist must get numerous measurements on a single formulation to be satisfied that there is interpretable data.

6.3.2 Foam Formulation and Structure–Property Relationships

As discussed in Chapter 5, the properties of a foam are largely defined by the tests that are performed [29–33]. Two foams may feel identical to the touch but perform very differently in tests developed to measure the same property (such as compression set). In addition, subtle changes in test conditions can reveal significant differences in foam performance (Fig. 6.12). This unavoidable fact regarding foam properties

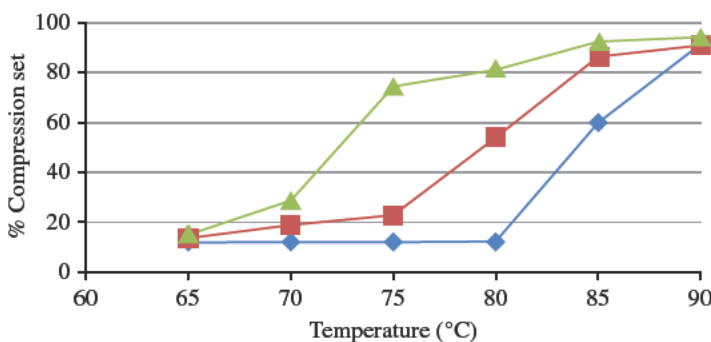


FIGURE 6.12 Compression set for three molded foams measured following 75% compression for 22 h (see ASTM 3574). All foams were four parts water and 105 index. The data shows the sensitivity of foam performance to structural details, as well as the importance of careful control of temperature when making these measurements since errors or large fluctuations can result in artifacts in the data. Reprinted with permission from Ref. [34]. © Elsevier Pub.

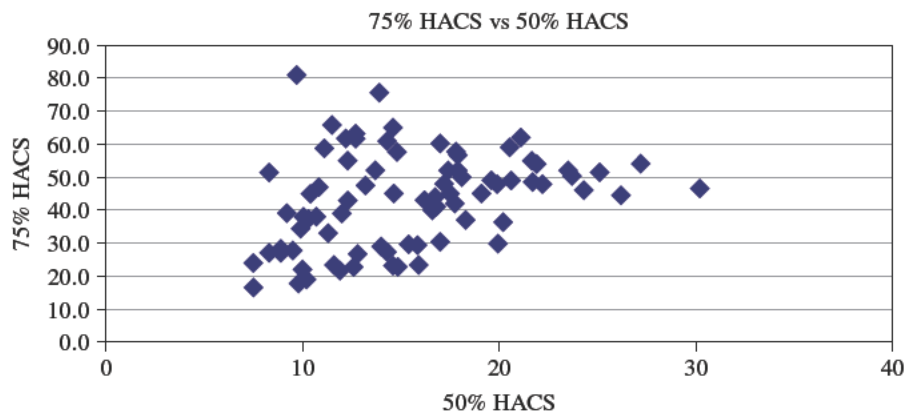


FIGURE 6.13 Lack of correlation of 75% humid aged compression set (HACS) with 50% HACS for MDI molded foams. The two compression tests sample mostly different physical properties of the foam. Reprinted with permission from Ref. [27]. © Elsevier Pub.

accentuates the need for very strict control of polymerization conditions to obtain optimized results. Additionally, it points out the need to make very careful measurements, especially with respect to temperature calibration since foam properties can have very nonlinear dependency.

It is generally conceded that the effect of formulation changes is the effect of those changes on the underlying structure as defined by the phase diagrams and phase separation mechanisms that determine that structure [27, 35]. Thus, if a test to measure humid aged compression set is performed at 50% compression, the result may not correlate at all with the same measurement at 75% compression. In fact, it has been demonstrated that the 50 and 75% compression tests do not correlate at all in molded foams (Fig. 6.13). While it is possible to pick points from the data set that appear to show correlation, it is clear from the analysis of large data sets that these measurements probe different aspects of polymer structure. A 50% humid aged compression set may probe the ratio of loss modulus to elastic modulus or the stickiness of the humid aged foam walls, while the 75% compression set measurement may probe the cocontinuity of the hard segment structure and its ability to regain its initial topology within the foam following severe deformation stresses. By the same token, different tests that do probe the same physical characteristics of the foam will correlate to each other, but not show correlation to a measurement that probes a different physical quantity. This is well illustrated by Figure 6.14 in which foam humid aged load loss (compressive softening to 75% compression after exposure to humid heat) correlates very well to 75% compression set but not at all to 50% compression set. As part of this analysis, it has been shown that the foam structural property that correlates to these measurements at high deformation stresses is in fact the hard segment thickness as measured by the SAXS-determined d-spacing (Chapter 5) (Fig. 6.15).

Finally, it is necessary to reiterate that the effect of formulation variables on foam properties is primarily a reflection on its affect on the foam's polymer structure. This

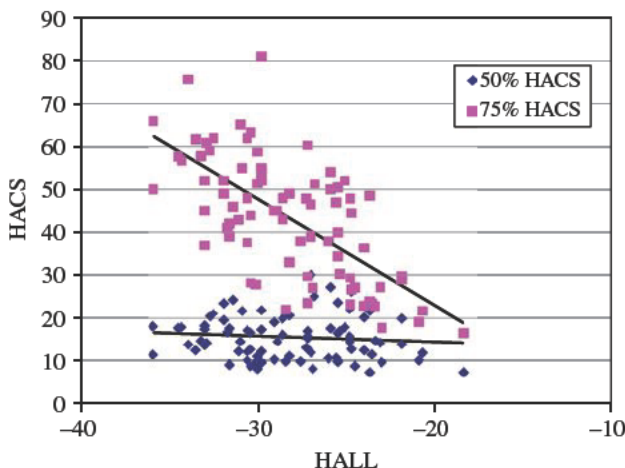


FIGURE 6.14 Correlation of humid aged load loss (HALL), a test that ages the foam in humid conditions and then tests compression resistance to 70% compression versus humid aged compression set (where the foam is maintained in a compressed state for an extended period of time and then removed from compressive strain and allowed to relax to an equilibrium thickness). The two tests that probe at similar strains are highly correlated to each other. Reprinted with permission from Ref. [27]. © Elsevier Pub.

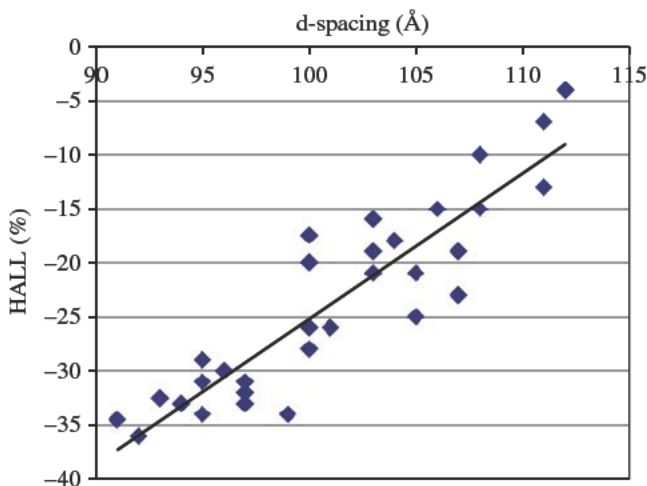


FIGURE 6.15 Correlation of humid aged load loss (HALL) to the small-angle X-ray-determined d-spacing (see Section 5.2.3). All foams have the same hard segment volume and demonstrate that the better the microphase separation, the better the aging properties when all other factors are controlled. Reprinted with permission from Ref. [27]. © Elsevier Pub.

is easily demonstrated by the lack of relationship between the content of DEOA, a polymer cross-linker, and a foam aging property such as humid aged load loss in the absence of control of other structural variables (Fig. 6.16). While it may be possible to perform an experiment in which the progressive addition of DEOA can affect foam

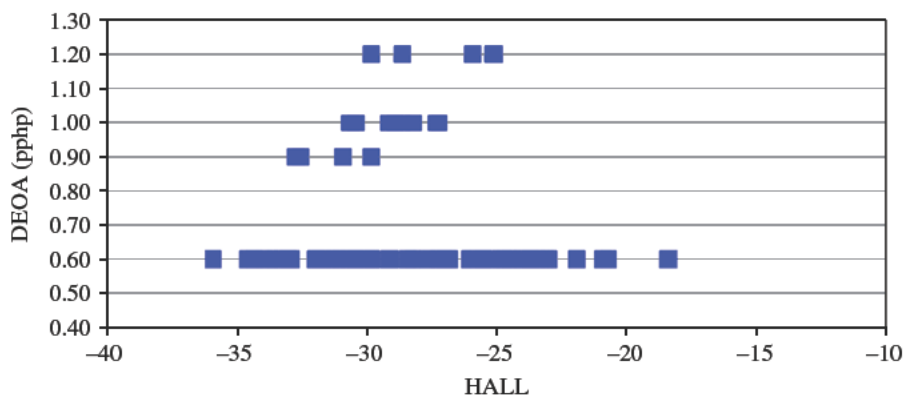


FIGURE 6.16 Lack of correlation of diethanolamine (DEOA, a cross-linking agent that speeds gelation) content in foam formulation and humid aged load loss. DEOA is a casual, not a causative, factor to aging properties. Reprinted with permission from Ref. [27]. © Elsevier Pub.

properties, it must be remembered that the effect of DEOA is actually a measure of its effect on the foam kinetics and resulting polymer structure, which in turn are directly responsible and not casually responsible for foam performance.

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7

POLYURETHANE FLEXIBLE FOAMS: MANUFACTURE, APPLICATIONS, MARKETS, AND TRENDS

Inspection of available data suggests that aggregate demand for polyurethanes is easier to determine than volumes based on application (i.e., flexible foam, rigid foam, elastomer, etc.) and by region. Chapter 2 provides regional volume production estimates for polyurethane building blocks. This data is presumably easier to obtain since significant producers tend to be large multinational publically held companies that are required to report their manufacturing data. The building block outputs can then be cross-referenced against the feedstock inputs that are also data that is available in the public domain. This same information is not readily available for foam producers. Part of this is because there are thousands of such producers [1]. Producers tend to locate their foam production facilities relatively close to the next-in-line manufacturer within the value chain (i.e., furniture, automotive seating, mattresses, etc.). Furthermore, foam producers are a mix of smaller publically held and privately held companies and can be highly economically sensitive. The economic downturn of 2008–2009 saw even relatively large foam producers enter into bankruptcy proceedings [2]. An aggregate of volume estimates of the flexible foam market in 2012 and projected growth rate broken down by geography for 2012 and 1991 is shown in Figure 7.1. The growth rate is of course merely suggestive, based on extrapolation from previous production/consumption volumes. Furthermore, within each geography, the growth rate may be highly variable with China, for instance, having an expected near double-digit growth in the consumption of flexible foams, while it is anticipated that Japan will experience near-zero to slightly negative growth in the flexible foam segment [3]. This historical discontinuity is dramatically shown in the

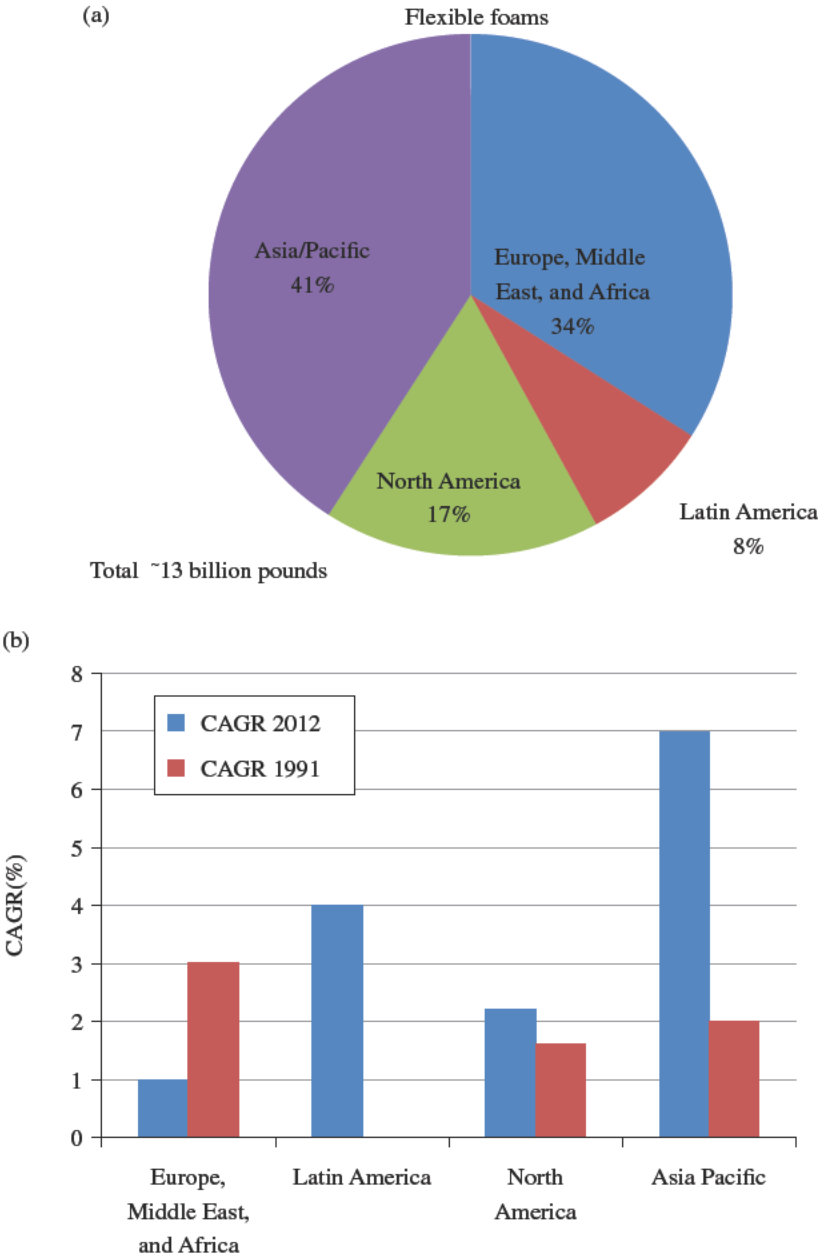


FIGURE 7.1 Approximate volume breakdown for the production (a) of polyurethane flexible foams by geographical region for the year 2012 and (b) the compound annual growth rate of flexible polyurethane foam production for the years 1991 and 2012. History can be a guide for the future, but extrapolation becomes less reliable the greater the distance from the reference year. (See insert for color representation of the figure 7.1(b).)

data on Asian growth rate, largely reflective of Japan's consumer demand in 1991 and of China's in 2012. Furthermore, there is paltry data on Latin American demand for 1991, while in 2012 it reflects a substantial proportion of the total. This chapter will cover the flexible foam markets, commercial considerations, and future trends based on data collected from the past 13 years.

The maturity and complications associated with the flexible foam market belie the relatively prosaic nature of flexible foams and their range of applications. In general, flexible foams are associated with their ability to provide cushioning and comfort. Thus, they find large-volume uses in furniture cushions, mattresses, automotive seating, carpet underlayment, clothing, and packaging [4].

7.1 APPLICATIONS

Although applications for flexible polyurethane foams are well enumerated, the relative volumes broken down by geography and foam characteristics are difficult to obtain with accuracy. Problems in developing a coherent picture are in part a reflection of the shifting use of descriptors and their uses. For instance, it is conventional wisdom that foam producers are under pressure to provide consumers with the so-called "green" options for purchase. This is commonly understood to mean that the foam is based on feedstocks from agricultural rather than petrochemical feedstocks. While several agriculturally based polyurethane feedstocks have come on the market, it is doubtful that the consumer is yet driving buying decisions based on feedstock origins. Rather, the "green" technology market thrusts are largely based on governmental mandates surrounding air quality associated with volatile organic emanations from formed foam, the use of heavy metal catalysts, and supplementary blowing agents that may be employed to promote foam rise [5]. Additionally, and specific to flexible polyurethane foams, there is a technology drive to implement flame retardant solutions that do not involve the use of halogens [6]. Recently, the use of phosphorus-containing flame retardants has also come under scrutiny [7]. In 2011, there was also action by the U.S. Environmental Protection Agency to explore restrictions of isocyanates in some applications [8]. European regulators have developed regulations that make automotive manufacturers liable for disposal of scrapped vehicles [9]. This burden has instigated activity for recovery and recycle of automotive polyurethane components. From the manufacturer's perspective, the drive is to provide equivalent cushioning and durability at lower densities translating to lower costs.

The breakdown of volumes applied to the various applications is also difficult to obtain, presumably because of poor tracking and a lack of motivation for data collation. A survey of data available for the United States is provided in Figure 7.2. Due to macroeconomic factors, as more chemical and end-use manufacturing is shifted to low-cost environments, the overall numbers can be expected to be volatile. While manufacturing may be shifted, it is likely that the snapshot provided in Figure 7.2 represents an equilibrium comparison between relative volumes required by mature economies for the various segments. A survey of similar data for 2005 [10] provided different absolute values but substantially similar relative numbers.

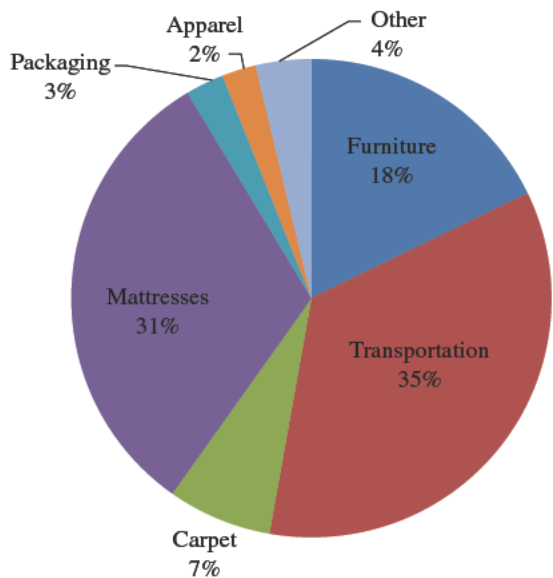


FIGURE 7.2 Approximate breakdown for the volume usage of flexible polyurethane foams in the United States for the year 2010.

7.1.1 Furniture

Application of polyurethane flexible foams for furniture is a highly economically sensitive segment that follows the overall housing market [11]. The furniture segment uses flexible foams obtained from both slabstock and molded foam operations. However, with furniture manufacturing shifting to low-cost environments and the cost competitive nature of the furniture market, there is a significant concentration of furniture foams made in lower-cost slabstock operations (Fig. 7.3). Examples of simple high-resilience slabstock formulations and properties are shown in Table 7.1.

The indentation force deflection (IFD; Table 7.1, Fig. 7.4) measurement is a test that is unique to the comfort segment. This is not a test with a clear relationship to fundamental aspects of polyurethane structure or chemistry. It is an application test with a direct correlation to how the foam is used (usually sat upon). The test is specified in ASTM D3453 and D5672 [12]. A foam sample that is approximately the size of a furniture cushion is compressed by a standard size circular press as shown in Figure 7.4. Manufacturers of end-use products specify the performance of the foam in this test, and the formulator and foamer will then design the foam to meet the test requirements. The specifications are usually the force measured by the df load cell at a certain compression or several compressions (i.e., 25, 40, and 65% compression). The force value is normalized to the foam density. Careful experiment will also normalize the compression response to airflow or at least assure that all compared foams have nearly the same airflow to prevent the measurement being influenced by hydraulic resistance (see Section 4.2.2.2). The foam designer will adjust airflow

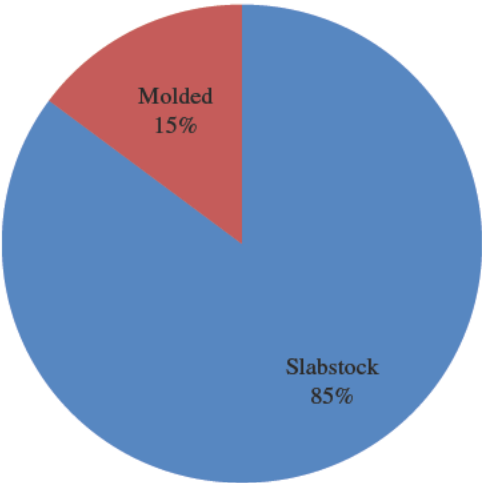


FIGURE 7.3 Approximate split for the polyurethane flexible slabstock and flexible molded foams in North America for furniture for the year 2010.

TABLE 7.1 Simplified formulation and representative properties for high-resilience foam for furniture applications at three different foam densities

	pphp	pphp	pphp
Sorbitol-initiated polyol	100	100	100
EO-capped OH 29			
Water	4.5	4	3
Diethanolamine	2	1.5	1
TDI index	100	105	105

Density	lbs/ft ³	1.26	1.56	1.87
IFD 40%	lbs	13.2	15.4	19.3
Resilience	%	60	60	62
Compression set	%	10	8	5
Elongation at break	%	150	135	120

Generally, the higher the foam density, the firmer and more durable is the cushion.

properties by careful balancing of diethanolamine cross-linker, gelation, and blow catalysts within the formulation. An additional industry specification gauged from this test is the so-called “sag” factor or comfort factor calculated from the ratio of IFD at 65 and 25% compression. Some manufacturers will use alternative ratios or limitations when using these terms.

All polyurethane markets are competitive, and the furniture market may be especially so [13]. Producer prices are always critical to market and manufacturer



FIGURE 7.4 Test fixture and sample geometry for testing flexible foam indentation force deflection (IFD), a common test for furniture applications. Image courtesy of Instron Corporation.

success, but intense competition assures that competent players rapidly respond to price changes in the market. Success in the furniture market usually requires an ability to meet all the customer requirements. Successful building block and foam manufacturers are able to produce the range of materials required by the next level in the value chain. The occasionally small-volume demands of particular applications have spawned the development of “system houses.” These businesses occupy a middleman position between the large building block producers and foam manufacturers. The system houses rapidly develop formulations that meet the small-volume applications required by the foam manufacturer. From the market perspective, the system application must demand and justify the increased price of specific formulation development. The success of system houses has inspired some large building block manufacturers to invest in or purchase their own system companies.

Success in the furniture market also requires that suppliers within the value chain have credibility and historical position within the market. Intuitively, it is clear that customers prefer suppliers with whom they have prior relationships and have a track record for delivering for the industry. This subjective requirement can act as a barrier to entry for new potential providers of products, as well as causing weakly positioned suppliers to fail when economic factors serve to differentiate among suppliers. In addition, history and position within the market provide the necessary up-to-the-minute intelligence of customers, competitors, and price for a rapid response to market demands and fluctuations. Lack of such information creates the so-called market

followers who traditionally exhibit poorer profitability even under the best of circumstances [14].

The furniture industry is not considered one that makes significant demands for new polyurethane technology. Price and regulatory forces are the main drivers of new products for this segment. Development of polyols from seed oil feedstocks has created some adjustment of formulations as furniture producers try to develop a market demand for “green” products. Some producers will substitute 5–10% seed oil-derived polyol for petrochemically derived polyol into their formulation. Larger additions are shown to deteriorate properties using low-cost substitutions [15, 16] or unacceptably raise prices for more capable seed oil-designed products [17].

Another area of technology development is the need for improved environmental health and safety of polyurethane foams. These issues relate to improved fire resistance and inhibited smoke generation from foams without the use of halogenated flame retardants [18, 19]. Second-choice flame retardants based on phosphorus are also potentially under scrutiny by regulators [20]. Reduction of volatile organic compounds from foams when in use is also considered a desirable feature by furniture manufacturers.

7.1.2 Mattresses and Bedding

As shown in Figure 7.1, mattresses and bedding (pillows, bolsters, mattress toppers) are a large and important industry segment for flexible foams. The market for mattresses is sensitive to the macroeconomic environment, and in some years, mattresses and bedding will in fact be the largest industry segment for slabstock foams [21]. The number of mattresses (and so volume of flexible foam) and the type of mattresses (better or poorer quality/more or less foam) will vary significantly from year to year. Mattresses and bedding are almost entirely based on slabstock polyurethane foam production. The types of slabstock foams used, however, do cover a distribution of specifications and thus formulations.

In Figure 7.5, the category of viscoelastic foam (also called “memory foam”) is introduced, and this class will be fully developed in the following. The quality of the foam is in part a function of foam density. Many consumers will make an informed decision to purchase mattresses with higher-quality foam having experienced the permanent deformations of mattresses based on low-density/low-quality foam (Fig. 7.6).

Mattresses are engineered structures [22, 23]. They are typically an ordered array of metal springs (the inner spring) covered by several inches of polyurethane foam. Depending on the size and density of foam covering the inner spring, a mattress may contain 10 lbs of polyurethane foam. Some mattresses (both high and low quality) will employ a polyurethane core in replacement of the inner spring. A high-quality foam core may utilize foam density as high as 4 lbs/ft³.

Over the past decade, a significant segment for flexible foam growth has been viscoelastic foams [24, 25]. Unlike conventional or high-resilience foams that are valued for their high efficiency in immediately returning energy, viscoelastic foams have a delayed recovery to deformation and are also called “low-resilience foams.” They are also called “memory” foams because of their ability to retain the shape of what was just compressing them (Fig. 7.7). Given time, a viscoelastic foam will recover its

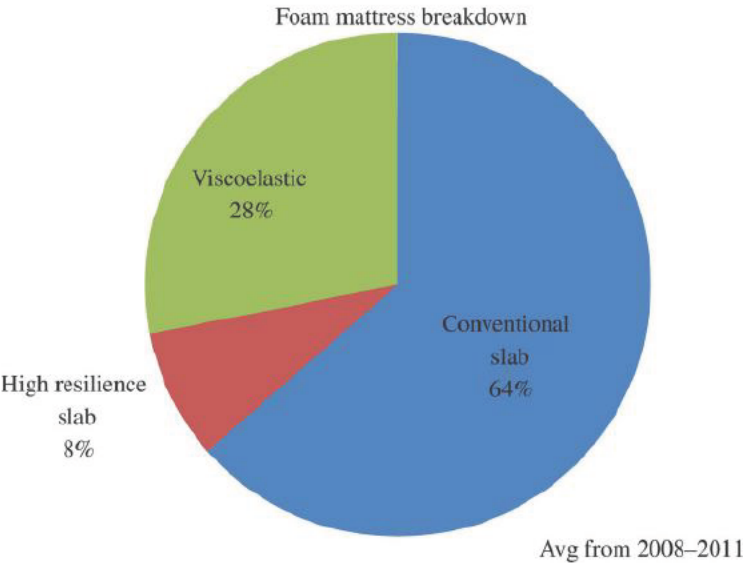


FIGURE 7.5 Approximate breakdown for the types of foams used in the manufacture of mattresses. All foams represent types of flexible slabstock foam manufacture.

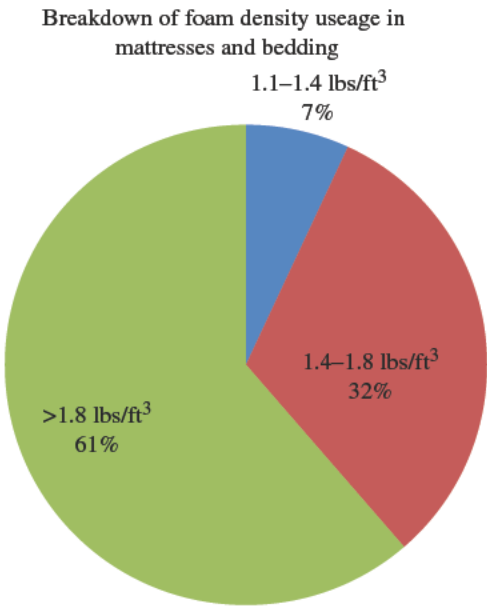


FIGURE 7.6 Approximate breakdown of the flexible foam market based on foam density. This data can fluctuate based on economic conditions with cheaper/lower density foams increasing in poorer economic conditions and more expensive/higher density foams increasing in better economic conditions.



FIGURE 7.7 Illustration of the delayed recovery response of a polyurethane viscoelastic foam. Image courtesy of The Dow Chemical Company.

original shape. The behavior of viscoelastic foam is a result of the underlying polymer structure and is controlled by the formulation that the foam designer utilizes. Specifically, when designing a viscoelastic polyurethane foam, the designer will formulate to result in a broad range of molecular weights between cross-links [26–29]. The effect of this molecular weight distribution is to broaden the glass transition temperature such that the molecular motions of the polymer chains have a broad range of relaxation times. In Chapter 4, the effect of block copolymer structure on the glass transition temperature was discussed, but the effect of cross-link density on the glass transition temperature of a rubber is roughly given by Equation 7.1 where M_c is the molecular weight between cross-links and k can be treated as a constant [30]:

$$T_g(n) \sim T_g(\infty) \times \left[1 + \frac{k}{f(M_c)} \right] \quad (7.1)$$

Thus, as the molecular weight between cross-links evolves to a broad distribution, the glass transition temperature will likewise reflect the breadth of that distribution. This will be reflected phenomenologically as a slow recovery of shape after deformation, particularly when the T_g is peaked between 0 and 15 °C (Fig. 7.8). Rheologically, the glass transition temperature reflects the physically encumbered chain motions being activated over a broad range of temperatures. From a foaming point of view, the broad and elevated tan delta slows the foam rise and cell reticulation (“blowoff”) since the low molecular weight between cross-links will enhance gelation over blow reactions. The result can be reduced airflow of viscoelastic foams due to a greater number of intact cell windows (Fig. 7.9). The reduced airflow can contribute to the slow recovery response of the viscoelastic foam, but its contribution usually evolves as the foam ages. From the manufacturing point of view, the production of viscoelastic foam is not different from the production of other slab foams except that the

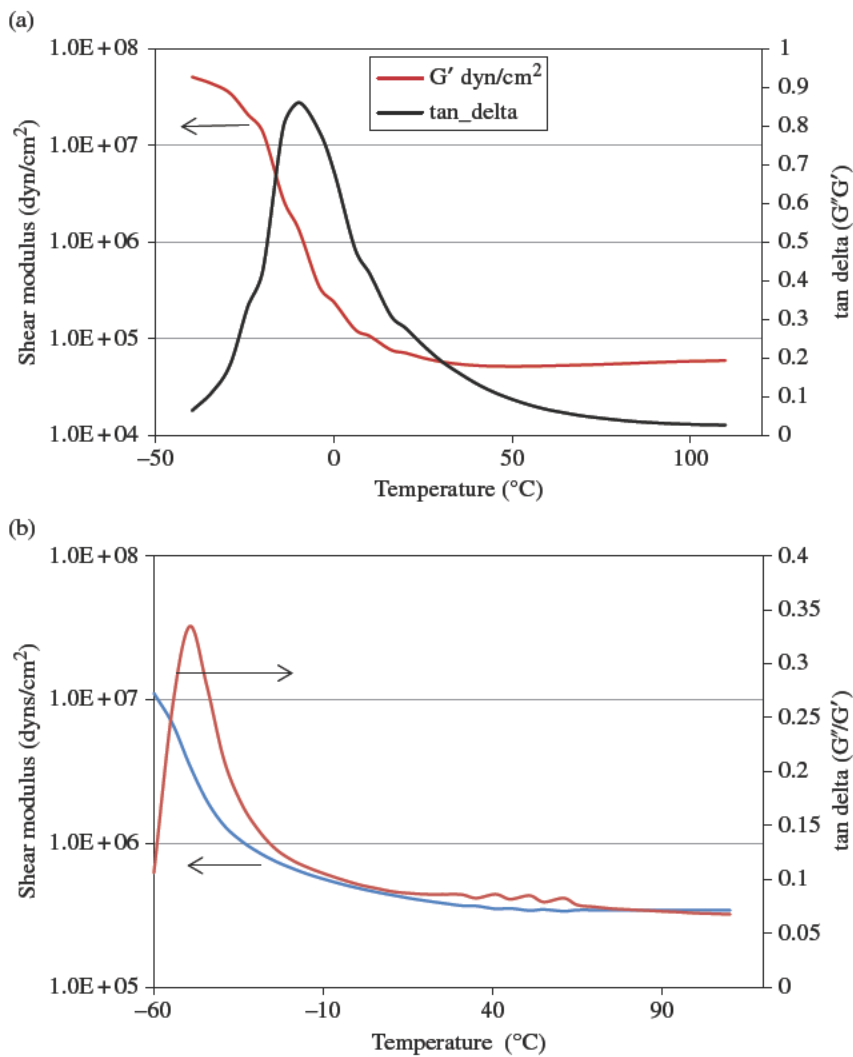


FIGURE 7.8 Shear modulus and tan delta spectrum of (a) a viscoelastic and (b) a comparative high resilience flexible foam. The position, width and amplitude of the tan delta peak are typical of those whose applications demand viscoelastic response.

designer will produce the desired effect by blending two polyols with substantially different equivalent weights. For instance, in the representative formulation of Table 7.2, one polyol has a hydroxyl equivalent weight of about 140 g/eq, while the other is approximately 1000 g/eq. Miscibility of the polyols assures that there will be a broad distribution of molecular weights between cross-links. While viscoelastic foams have by far made their largest impact in mattresses and bedding, they are beginning to appear in some automotive seating systems as foam designers have learned to broaden out the tan delta envelope to the required temperature range specified by manufacturers [31].

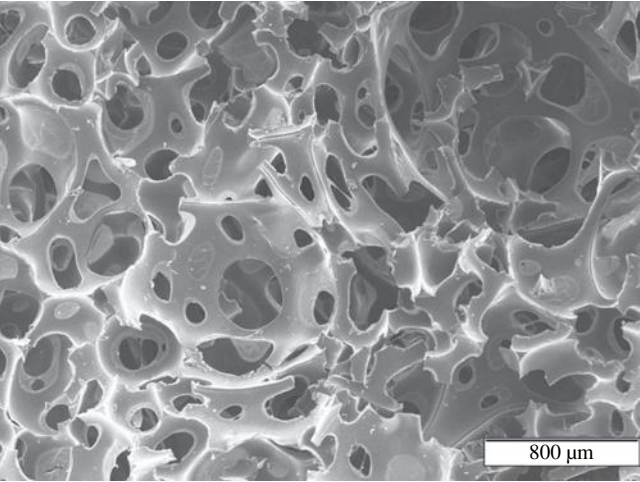


FIGURE 7.9 Scanning electron microscope image of a typical viscoelastic polyurethane foam.

TABLE 7.2 Representative formulations and property ranges for viscoelastic foams prepared at three different densities

Component	2.5 lbs/ft ³	4 lbs/ft ³	6 lbs/ft ³
Glycerine-initiated PO triol, equivalent weight 140 g/eq	75	70	70
Glycerine-initiated PO triol, equivalent weight 1000 g/eq	25	30	30
Water	2.6	1.4	0.8
Silicone surfactant for viscoelastic foam	1.3	1.1	0.7
Tin (II) catalyst	0.09	0.05	0.03
Balanced amine catalyst for slabstock	0.7	1.5	1.9
TDI index	87.5	87.5	87.5

Foam property	Value range
Density (lbs/ft ³)	2.5–6
IFD at 25% (lbf)	13–45
Recovery time (s)	2–15
Resilience (%)	2–10
Compression set at 75%	<10

7.1.3 Transportation

Over 75% of flexible foam products targeted at the transportation market are designed for seating within automobiles, buses, trucks, airplanes, etc. [32]. Additional areas employing flexible polyurethane foams are instrument panels, headliners, door

panels, arm and head rests, and also within structural members for the purpose of noise reduction. Each application has specific requirements that are met by specific and highly optimized formulations.

As mentioned in Chapter 6, the comfort aspects of seating are subjective, and different world geographies have consistently developed formulations that reflect these preferences. Thus, the North American market typically seeks greater softness in seating, translating to lower-density TDI-based foams. The European market has generally delivered firmer seats using higher-density foams based on MDI. The Asian market has generally sought a middle ground between these consumer expectations [33]. In this regard, the aging demographics of the traveling public have evolved over time to seats that offer firmer support in seat backs. Due to the importance of seat comfort to the purchasing decision and the perception of delivered comfort, automobile manufacturers have specific standards that foams must deliver in every aspect of their static, dynamic, and aging properties. Furthermore, the specifications for driver, front passenger, and rear seats are usually different and in order of declining quality [34].

Given the proliferation of specialty polyurethane foams sought by manufacturers and consumers for transportation applications, the best that can be offered are representative recipes for foams that have a good chance of working in typical equipment. While some transportation applications such as carpet underlay and headliners can be made from slabstock foams, almost all seats are prepared by molded foam operations. The specificity of molding equipment is an additional overlay of complexity in creating useful foam since different molding equipment may produce somewhat different foams with the same polyurethane formulation [35–37]. Table 7.3 provides a representative molded foam formulation based on TDI, molding conditions, and properties for an automotive seat cushion that might be found on a car manufactured in the United States.

An MDI-based molded foam formulation is presented in Table 7.4. While the conditions and results are somewhat different than those of the TDI foam of Table 7.3, these distinctions should not be viewed as a general representation of the differences. The opening and demold times can be as much about arbitrary process differences as about demands resulting from the specific formulation. Molded foam operations also commonly use prepolymers (Section 2.1.7) rather than pure pMDI/isocyanate monomer mixtures. The prepolymer route may ease certain process requirements related to mixing, pumping, and mold filling, justifying the added complexity and expense of employing a prepolymer.

While the formulation choices and foam property variability can be mind-boggling, there are a few general rules for molded foam types and compositional choices (Table 7.5) and formulation variables and their effects on molded foaming and molded foams (Table 7.6).

7.1.4 The Molded Foam Market

The dominance of the molded foam business by the transportation sector results in a unique commercial structure. The *slabstock* flexible foam market is highly driven by price, supply reliability, and the mutual interest of a varied and highly fractured foam market to absorb the high-volume output of an asset-driven, concentrated polyurethane building block industry. While the *molded* foam market is also highly price sensitive, it is equally driven by the competition between commercial relationships. Additionally,

TABLE 7.3 Representative formulation, molding conditions, and properties of a high-resilience TDI foam that might be utilized for a seat cushion in the U.S. transportation market

Component	pphp
3.8 functional (sucrose/glycerine mixed initiator 1730 hydroxyl equivalent weight 16% EO-capped PO polyol	75
40% SAN 2500 equivalent weight copolymer polyol with similar composition to polyol	25
Water	2.8
Diethanolamine	1.75
Triethylenediamine (gelation catalyst)	0.3
(Dimethylaminoethyl)ether (blow catalyst)	0.7
Silicone surfactant	0.8
TDI	100 index

Molding: HiTech SureShot 50

Block size: 38 × 38 × 11.4 cm

Pad weight: 695 g

Mold temperature: 75 °C

Demold time: 3 min

A/B steam pressures: 2300/2400 psig

Test	Value
Density (kg/m ³)	42
Airflow (ft ³ /min)	1.4
IFD 25% (kg)	10
IFD 50% (kg)	19
Resilience (%)	71
Humid aged compression set (%)	18

Note the exceptionally high resilience measured for this formulation.

there is the commercial tension brought on by low-margin large businesses (such as commodity producers) and the high cost of sales needed to supply specialized formulations for specific and niche applications. This conflicting need for price and specialization has resulted in the development of distributors who purchase building blocks directly from the building block manufacturer to service small accounts. Inevitable overlaps form with the range of direct sales from the major manufacturer and the distributors. In addition, specialization has also spawned the creation of formulation houses (or “system houses”) that simultaneously purchase polyols and isocyanates from building block manufacturers and at the same time compete with these same feedstock manufacturers at *customers* using fully formulated systems. In response to these pressures, the large building block manufacturers have evolved by buying or developing their own distributor and formulation (or “system”) houses. Figure 7.10 provides a visual map of the relationship between the building block producers, distributors, and the formulation houses.

TABLE 7.4 Representative formulation, molding conditions, and properties of a high-resilience MDI foam that might be utilized for a seat cushion in the European transportation market

Component	pphp
2000 equivalent weight glycerine-initiated PO polyol 15% EO cap 80% primary hydroxyl	75
1675 equivalent weight glycerine-initiated EO/PO mixed feed polyol (primarily used to enhance cell openness)	4
Water	3.5
Tris(dimethylaminopropyl)amine balanced blow/gel tertiary amine	1
Low-efficiency silicone surfactant	1
Polymeric MDI: 2.7 functionality, 137 isocyanate equivalent weight, 31% isocyanate content	60
MDI 30/70 ortho-para'/para-para (index 105) (see Chapter 2)	40
Cannon Model A 60 w/FPL 18 mixing head	
400 g/s output	
2000 psi/2000 psi polyol/isocyanate pressure at 25 °C	
Mold temperature: 50 °C	
Opening time: 3 min	
Demold time: 4 min	
Test	Value
Density (kg/m ³)	51
Resilience (%)	57
IFD at 25% (kg/m ³)	
Dry compression set (%)	7
Humid aged compression set (%)	13
Ultimate elongation (%)	100

Pertinent differences relative to the TDI foam of Table 7.3 are the density, resilience, and IFD.

TABLE 7.5 General formulation guidelines for transportation seating molded polyurethane foams according to the isocyanate classification

Foam type	Clear polyol equivalent weight (g/eq)	% solids in polyol–copolymer blend	Isocyanate
Hot cure	1000	0–25	TDI
HR iso blend	1600–2300	5–35	TDI/pMDI
TDI HR	1600–2300	5–35	TDI
MDI HR	1600–2300	0–20	pMDI/MDI or prepolymer

TABLE 7.6 General structure–property relationships for flexible molded polyurethane foams related to choice of polyols

Formulation variable	Effect
Increased hydroxyl equivalent weight	Increased viscosity, increased elongation at break, increased resilience, lower load bearing
Increased polyol functionality	Increased viscosity, increased load bearing, lower elongation at break, lower compression set, lower airflow, increased durability
Lower monol content	Lower hysteresis, lower compression set, less vibration conduction, increased durability

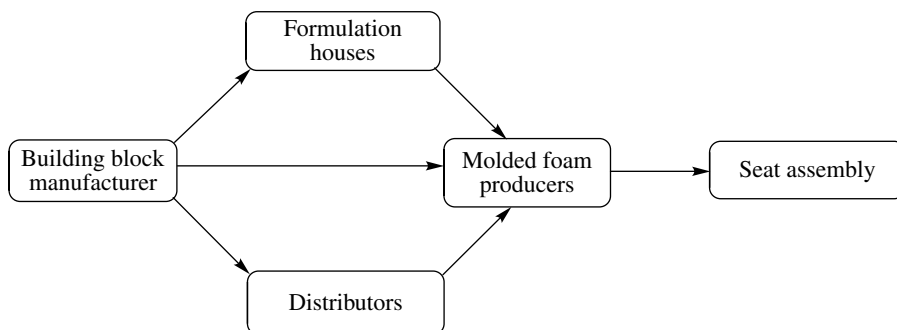


FIGURE 7.10 Unique commercial relationships among suppliers to the transportation seating market. This situation is bound to evolve, but which channel prevails will depend on unforeseeable market and macroeconomic factors.

7.2 TRENDS IN MOLDED FOAM TECHNOLOGY AND MARKETS

While the patent literature is notably poor at providing insight into fundamental science, it is the clearest way to understand the future of a technology and market [38, 39]. This is because the patent literature represents a sizable investment by a company or individual on what is believed will be desirable by customers and market competitors in the next-generation product. Furthermore, defense of a patent asset requires that the technology on which a patent is based be protected by patent prior to its commercial introduction.

While a single patent may not be instructive as to the direction of future innovation, a clear trend in industrial patent activity can be unmistakable. Figure 7.11 shows the patent activity of several large multinational polyurethane feedstock providers over the years 2000–2013. In this analysis, the patents filed in the Chinese language represent the activity within the sizable Chinese market by Chinese companies. For perspective, the total number of issued patents found within the search parameters was 1033, so it is clear that there are a large number of patents not accounted for by this analysis. Despite this, it is likely that the preponderance of unaccounted for patents will reflect the activity of these highly experienced and influential participants (i.e., Dow, BASF, and Bayer) within the polyurethane market. Figure 7.11 shows that the majority of issued patents reflect the attempt to protect novel flexible foam properties and processes for a specific formulation or range of formulations. Arguably, this is suggestive of the richness of polyurethane chemistry and the fact that creative scientists are still finding new ways to achieve continuous improvements. However, it can also be argued that these patents cannot be considered as part of a more general future-oriented strategy since they reflect the properties found in pursuit of current applications. However, within this category, there are also industrial trends.

Relative to foam properties, innovation is being pursued to provide thinner/lighter seat foams with identical support properties achieved by thicker/heavier foams. Some of this activity is being motivated by the desire of automobile manufacturers to provide lower-profile automobiles for improved wind resistance without sacrifice of occupant headspace. The advent of hybrid and electric vehicles also has created a premium for space that can otherwise be utilized to hold batteries.

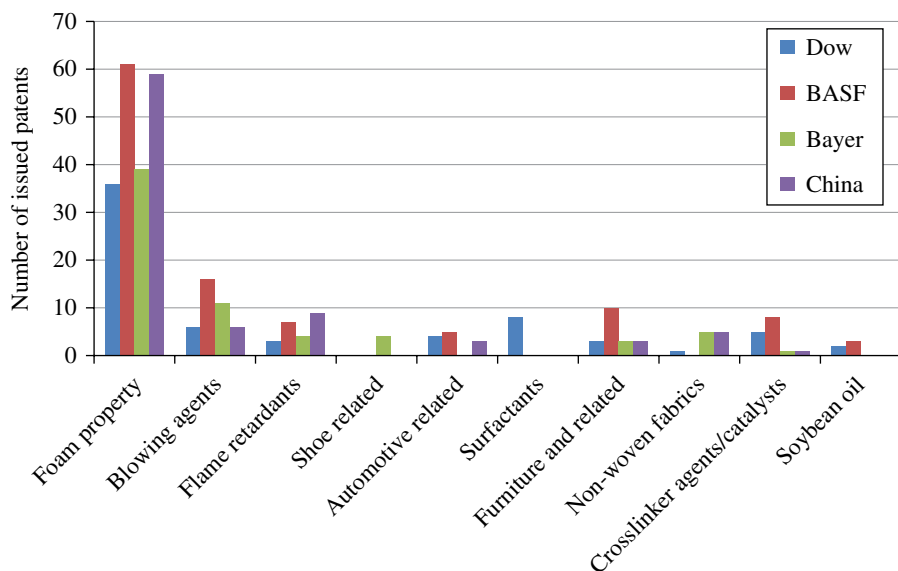


FIGURE 7.11 Patent activities within flexible polyurethane foam category of several large polyurethane market servicers and the patents filed in the Chinese language for the years 2000–2013 over the years 2000–2013. (See insert for color representation of the figure.)

Another foam property trend is the desire to provide foam that maintains a high level of support and comfort and at the same time dissipates vibrational energy that may otherwise be transmitted through the seat and degrade the perception of comfort. The balance is that many support and durability factors are highly correlated with low hysteresis. Low hysteresis, a result of network connectivity and phase separation, which results in low energy loss upon compression, works against vibration damping. Foam innovation has resulted from the identification of those vibrational frequencies that are perceived to result in passenger discomfort. It has been established that discomfort is perceived at vibrational frequencies less than 6 Hz [34, 40–42]. Thus, foam innovation has focused on development of foams that under compression dampen frequencies below 6 Hz.

We can understand the innovations of tailored foam vibrational damping by consideration of the equations relating mechanical properties to vibration transmissivity (Eq. 7.2) [43–45]. In Equation 7.2, K is the dynamic spring constant or stiffness (units of N/m), g is the gravitational constant (m/s^2), W is the applied load (N), and C is the damping factor (N-s/m). From the perspective of designing a polyurethane foam to achieve a desired result, it is simplified at least to the extent that the only variable that can be impacted by formulation is K , the foam stiffness. The foam stiffness is a function of many possible design variables and would have to be optimized within the boundaries of all of the other critical foam performance criteria. From the processing perspective, the damping factor can be influenced by foam structural properties like pneumatic damping, suggesting that optimization of airflow resistivity can help to increase vibrational damping. Alternatively, the tan delta spectrum can be optimized such that certain relaxation modes are inhibited at typical driving temperatures to retard energy return of certain frequencies (i.e., under 6 Hz)

to the driver. This technique would have to be balanced with the comfort perception that highly resilient foams are closely associated with passenger comfort in the absence of vibrations:

$$\begin{aligned}\text{Resonance frequency} &= \frac{1}{2} \pi \sqrt{\frac{Kg}{W}} \\ \text{Amplitude factor} &= \frac{1}{C} \sqrt{\frac{KW}{g}}\end{aligned}\tag{7.2}$$

Figure 7.12 provides the same information subtracting the patents protecting a specific foam property but instead focusing on a general field of application or composition of matter. This analysis shows that the most active fields of patent activity are those guided by regulatory pressures associated with supplemental blowing agents and flame retardants. A somewhat hidden patent field is the catalyst category. The import of this activity is apparent by the fact that all companies are engaged, in spite of the fact that these companies are not specifically catalyst manufacturers. Their presence in this field may point to anticipated regulation by occupational safety and health agencies of certain catalysts like those based on tin and mercury [46, 47].^{1,2}

Across the rest of the spectrum of activity, it is apparent that an individual company may pursue a specific intellectual asset strategy independent of the activity of its peers. Activity by a few companies in the use of soybean oil is a reflection of a strategy of pursuit of that agricultural oil as an alternative feedstock. However, the fact that not all companies are active in that area may suggest that not all companies share a soy-based-alternative-feedstock-for-polyurethane vision or may be taking a strategy of waiting to see if alternative feedstocks come to commercial fruition before developing a market follower technology response. Several companies, including Bayer and BASF, have also pursued an alternative feedstock vision employing ricinoleic acid (from castor beans; see Chapter 2), which has intrinsic secondary hydroxyl groups along the triglyceride chains. While ricinoleic acid has a process advantage by not requiring industrial introduction of hydroxyl groups onto the backbone, there is at least one serious disadvantage associated with a ricinoleic acid strategy for feedstocks (except for very small applications). Specifically, it relates to the limited volume of castor oil (the source of ricinoleic acid) in the world. Difficulty in growing and harvesting castor oil has narrowed the number of producing countries to primarily India and secondarily Brazil. The annual volume of produced castor oil is less than 2 billion pounds [48]. While this sounds like a lot, available volume is relatively in short supply compared to alternative agricultural oils like soya or canola.

¹Di-octyl tin catalysts are currently classified as category 3 substances—a substance of concern for humans because of possible CMR (carcinogenic, mutagenic, or reprotoxic) effects but for which there is not enough information available to classify these substances and preparation into category 2 (a substance of very high concern) status. European Commission Decision 2009/425/EC claims organotin compounds pose a risk to human health and will expand the scope of restrictions beyond those currently in place on maritime applications.

²European regulation under REACH (Regulation, Evaluation, Authorization, and Restriction of Chemicals) number 1907/2006 severely limits the use of organo mercury compounds such as PU catalysts.

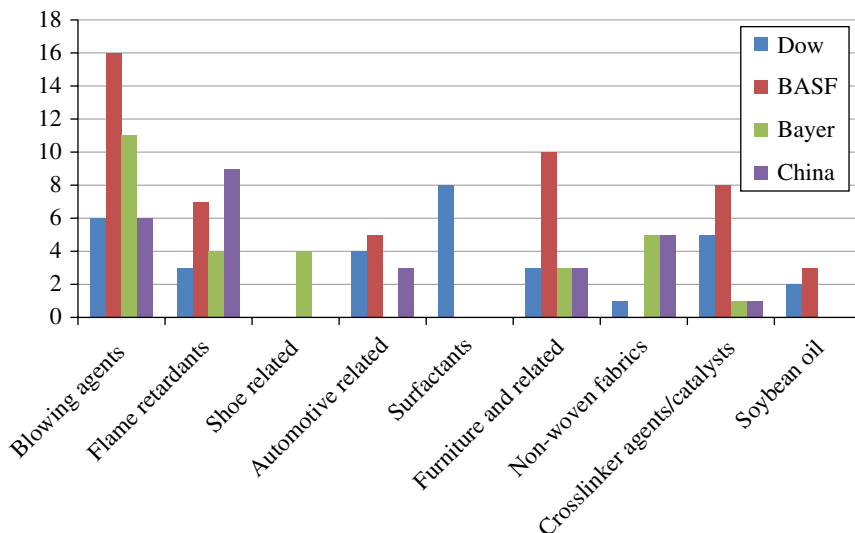


FIGURE 7.12 Data of Figure 7.9 with “Foam property” category removed to improve visualization of more specific subjects. (See insert for color representation of the figure.)

Acreage devoted to production is controlled by governmental agencies, and there is approximate balance between current supply and demand at relatively elevated prices. Accessing ricinoleic acid volumes required to satisfy an alternative feedstock strategy would distort the market for castor oil and raise prices—probably sufficiently to make the product economically untenable even with the lower capital cost allowed by an “isocyanate ready” triglyceride or source of fatty acid.

Lastly, over the years 2000–2013, it would appear that patent activity is relatively muted for such a large industrial segment and that BASF has been the most active company.

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8

POLYURETHANE RIGID FOAMS: MANUFACTURE, APPLICATIONS, MARKETS, AND TRENDS

About 50% of all polyurethane foam production is consumed by market demand for rigid polyurethane foam [1]. In contrast to flexible foams that are primarily an agent for comfort and cushioning, rigid foams are sought for their use in insulation and energy efficiency. To fulfill that mission, polyurethane rigid foam formulation, physics and methods, are very different from those for flexible foams, even while the fundamental aspects of chemistry, reaction kinetics, structure development, and morphology are the same. Polyurethane rigid foam is a premier material for delivery of insulation efficiency as illustrated by Figure 8.1 [2]. In contrast to other conventional materials, polyurethane provides the most insulation for unit thickness. As a two-component application, it provides flexibility to where and when the building blocks are transformed from liquid to solid foam form. Due to the large number of building blocks and the commodity nature of the feedstocks to make them, rigid foams can be produced at relatively low cost and able to provide a significant amount of differentiation to suit specific application requirements.

8.1 REGIONAL MARKET DYNAMICS

The estimated production of rigid polyurethane foams in 2012 is shown in Figure 8.2. Rigid foams primarily comprise (i) those produced for building insulation, primarily produced geographically close to where they are used, (ii) foams used for appliances that will represent the summation of regional consumption and those made for export. Many of the emerging economies are developing strong demand for

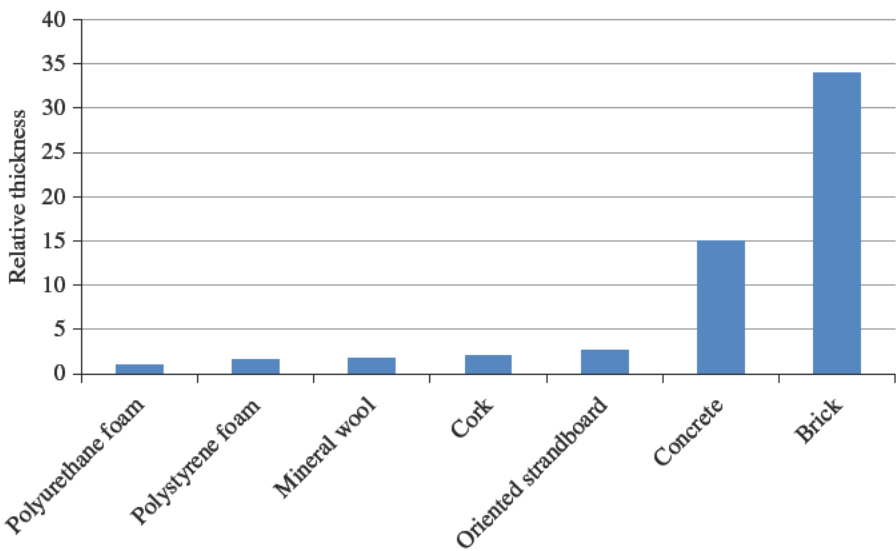


FIGURE 8.1 Relative performances of common insulation materials and construction materials. It takes more than 2 in. of cork and 15 in. of concrete to provide the insulation of 1 in. of PU rigid foam.

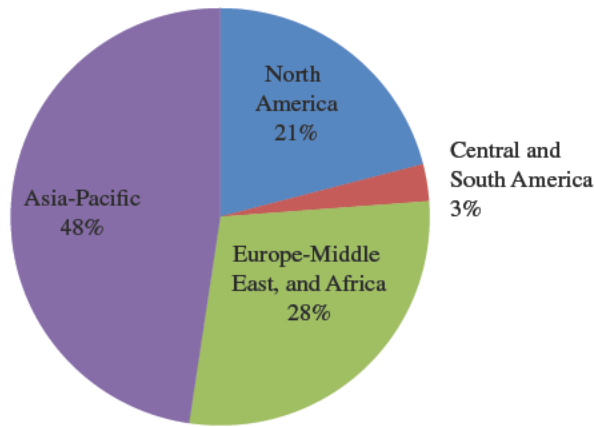


FIGURE 8.2 Proportional production of rigid foams in 2012 segmented by geographical region.

appliances such as refrigerators, but certainly much of the production in the Asia-Pacific region is for export to other geographies.

In mature economies such as those of North America and Europe, the production of rigid foam for construction is about double that produced for appliance applications. In the emerging export economies, the volume ratio of construction to appliance foams is close to 1, representing the overproduction of foams for appliances that subsequently get exported.

While useful, the data in Figure 8.2 is a vast simplification of a remarkably complex geographical puzzle. For instance, in the Asia-Pacific region, the polyurethane rigid foam market for appliances has many hundreds of foamers, but the top ten represent about 50% of the total volume. In that market, the local Wanhua Group dominates the local trade for building blocks to make rigid foams. Asian polyurethane producers monopolize about 50% of the total Asia-Pacific market for chemicals. All the large multinational companies have a footprint in the Asia-Pacific region with varying degrees of market penetration. As with many industries of which polyurethanes is an example, the power of a historical business relationship between two companies (i.e., supplier and customer) is as important in many ways as price, and it is known that certain suppliers have entrenched relationships with customers that are resistant to simple price inducement to switch.

For illustrative purposes, another fascinating dynamic of the Asia-Pacific market are the consequences of the phenomenal growth of these emerging and established economies [3]. In anticipation of the large Chinese population's demands for the conveniences and standards of modern life, there has been rapid expansion of industrial production. As Figure 8.3 shows, the supply/demand ratio for polyurethane chemicals has grown to an extent that industrial asset utilization is projected to be below 70% for many years—a value considered to be extremely low. It remains to be seen if such low return on investment can be tolerated by the industrial concerns, or if asset utilization will in fact accelerate and thereby help maintain a healthy and growing industry. In any case, it assures that basic costs for polyurethane chemicals in the Asia-Pacific

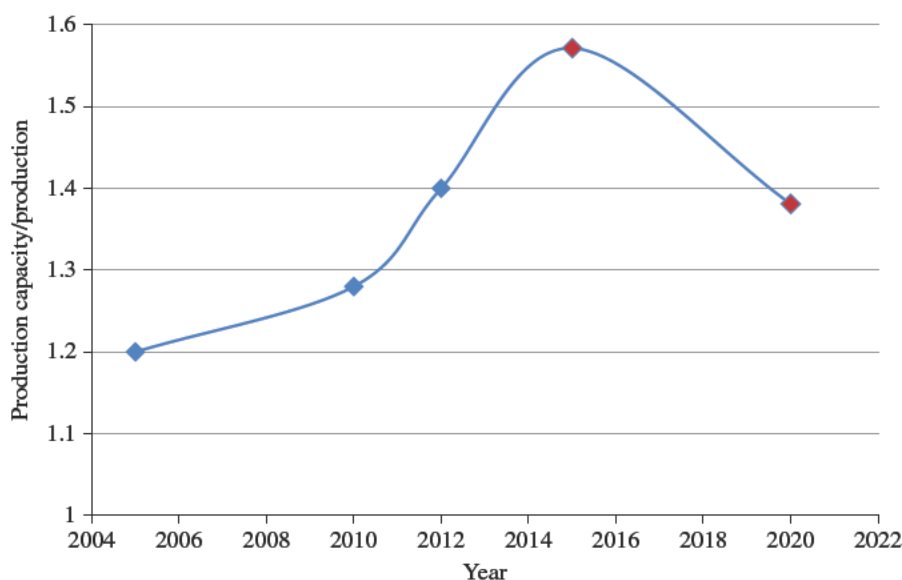


FIGURE 8.3 Ratio of production and consumption volume in the Asia-Pacific region showing the extent of regional investment in the polyurethane industrial base. ♦ Indicates a projected value.

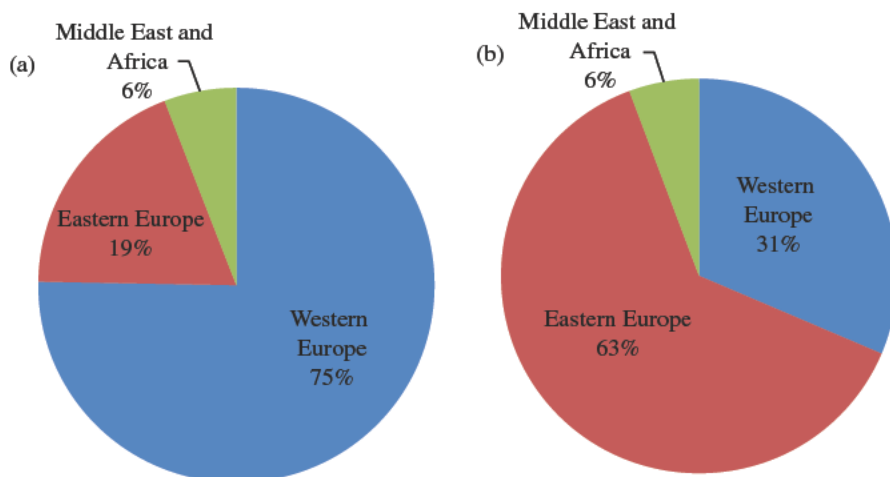


FIGURE 8.4 Approximate European (a) construction and (b) appliance market sizes for 2012. Total volume of construction market is approximately 1 billion pounds and about 500 million pounds for the appliance market.

markets will remain low, and will contribute to low price inflation from finished products using polyurethane products exported from these economies.

A more complex market situation is presented by Europe, Middle-East, and Africa. Beyond geographical proximity, this category is somewhat arbitrary with the Middle-East and Africa representing between 5 and 10% of the total addressable market for rigid polyurethane foams for this grouping [1, 4]. Within Europe, there is a bifurcation in market activity between Eastern and Western European markets (Fig. 8.4).

For rigid foam targeted toward the construction market, Western Europe represents about 75% of the total volume. This reflects greater emphasis on energy efficiency in the Western European construction market, and willingness of consumers to pay for benefits accrued to resource conservation. By contrast, the market for polyurethane foams directed at appliances is dominated by Eastern Europe with about 65% of the total addressable market. To some extent, this reflects the faster growth of consumer culture purchasing appliances, but also reflects the lower labor-cost environment of Eastern Europe attracting manufacturing assets for export to other geographies.

Like most Western economies, there is a high level of competition among multinational chemical producers. Unquestionably, the large German concerns, Bayer and BASF, dominate the European commercial landscape serving about 40% of the construction market and nearly 60% of the appliance market. To be sure, other companies including Dow and Huntsman compete with Bayer and BASF in the European polyurethane rigid foam markets. While the dominance of the German concerns may, to a small, extent reflect regional preference for a local producer, it also reflects the product mix Bayer and BASF offers that most closely suits the local requirements. Polyurethane chemical feedstock producers from China are also developing a

commercial presence in Europe, the main effect being to maintain a low-price environment for all competitors for the foreseeable future due to oversupply in Asia.

The North American market for rigid foams (including the United States, Canada, and Mexico) in 2012 totaled about 2.5 billion pounds. This volume is dominated by the US market (Fig. 8.5). The market dynamics are somewhat similar to those of Europe with the low labor cost Mexican economy producing a preponderance of appliance foams that then get exported throughout North America. Large multinational

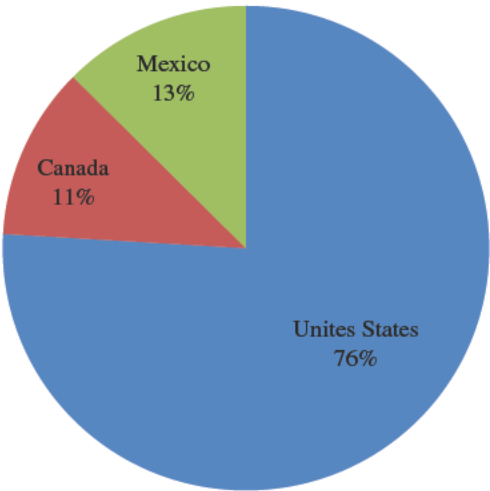
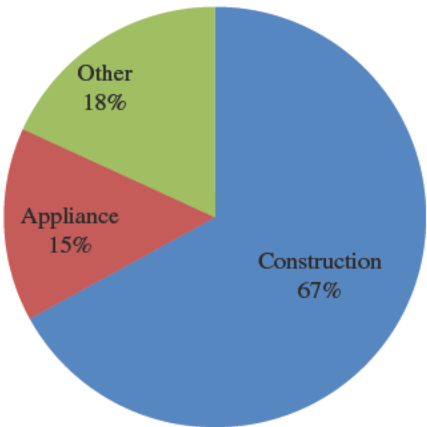


FIGURE 8.5 Approximate breakdown of the North American rigid foam market size. Total volume is about 2.5 billion pounds.

(a) The United States and Canada



(b) Mexico

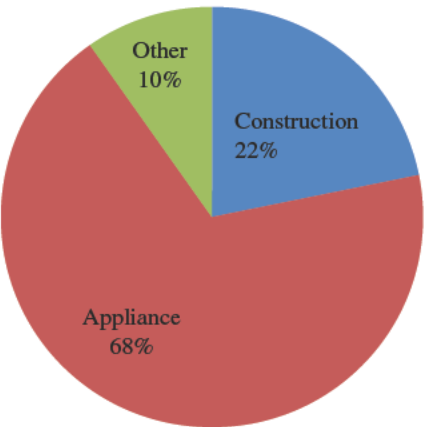


FIGURE 8.6 Proportional consumption of polyurethane rigid foams in (a) the mature consumer economies of the United States and Canada (b) the consumer/export economy of Mexico. “Other” represents automotive, pipe, packaging, and other smaller applications.

concerns such as Whirlpool, Samsung, LG, and MABE (a company indigenous to Mexico), are significant customers for appliance foams targeted for local, but primarily, export markets. The breakdown for market participation is provided by Figure 8.6. Canada and the United States are combined since their percentage breakdown by application is insignificantly different. The similarity between the participation of Eastern Europe and Mexico in their respective regions is striking and reflects their common participation roles in these markets.

8.2 APPLICATIONS

As mentioned in Section 8.1, the main use for rigid polyurethane foam is as a source of insulation. The primary industries utilizing rigid polyurethane foams are the construction and the appliance applications [5]. Even applications under the heading “other” in Figure 8.6 serve the purpose of insulation as used for pipe and tank insulations or insulation from vibration and noise when used in automotive cavity filling. The foam differences in these different applications are minor compared with the differences with for instance, flexible foams. The differences that do exist are a result of optimization for the purpose of meeting performance or processing requirements unique to the particular application. For instance, spray foam insulations must provide a high degree of flame retardance and very rapid gelation so that the spray insulation can be applied to vertical surface with minimal dripping or sag [6]. In contrast appliance foams must also form quickly, but not so quickly that the injected formulation cannot fill a mold cavity with any structural encumbrances to flow that may exist [7]. Further, appliance rigid foam must contribute substantially to the overall appliance structural stability, but not deform the appliance exterior in any way. Finally, as a widely used consumer material with energy-saving functions, polyurethane rigid foams have been the target of governmental regulation and performance requirements that have driven demand and innovation. The manner in which foam designers cope with these demands—some of these demands conflicting with each other—is discussed in the Sections 8.2 and 8.3.

8.2.1 Construction Foams

Rigid polyurethane foams used for construction purposes must serve the insulation and energy conservation goals of the application and not act in any detrimental way to the overall structural integrity of the building [8]. Construction is an immensely complex market [9], and the development of polyurethane rigid foams has proliferated several methods of delivering insulation properties to the building site. Polyurethane rigid foams are produced in composite panels, in two-component spray foams, and more recently in aerosol spray cans.

8.2.1.1 Polyisocyanurate Foams Virtually, all urethane-based boardstock used in the construction industry, especially when used for roofing or walls is based on polyisocyanurate chemistry [10]. The formation of isocyanurate structures is covered in

Chapter 3. A high functionality polymeric MDI is usually employed. It is used in large stoichiometric excess in the overall foam formulation to facilitate reaction of one isocyanate with another. Isocyanate reaction to form ring structures is further promoted by employing catalysts known for specifically forming isocyanurate rings as discussed in detail in Chapter 3. These catalysts are usually carboxylate salts or amine salts. Examples are, for instance, potassium octoate and the 2-ethylhexoate salt of 2-hydroxypropyltrimethyl ammonium. The catalysts act by strongly complexing the electropositive isocyanate carbon inducing a high enough negative charge at the isocyanate nitrogen to complex the carbon of another isocyanate propagating to an oligomer of 3 [11–13]. At that point, the six-member ring closes to form the ring structure shown in Figure 8.7.

The isocyanurate structure is particularly well suited to construction applications due to its inherently greater flame retardancy and thermal stability than possessed by urethane or urea crosslinks [14]. In addition, isocyanurate's high crosslink potential through structure (Fig. 8.7) creates a more rigid board structure. The high isocyanate content used in the formulations further creates the potential for very good adhesion to other components of a composite structure such as might be employed to make a sandwich panel. Such composite materials could be aluminum or steel facers and fiber glass mats for additional dimensional stability and fire performance [5, 15].

Table 8.1 provides representative formulations for isocyanurate polyurethane rigid foams. Formulation 1 is what might be well used in a commercial building and can be exposed to the building interior by virtue of the special design for flame retardance by using high levels of isocyanurate and added flame retardant. Formulation 2 is what might be utilized in residential insulation applications for external wall cavities. An aluminum-faced isocyanurate foam image is provided in Figure 8.8 showing the closed cells and the very thin aluminum facing employed for improved time dependence of the insulation properties and improved flame retardance.

The flexural modulus is also a measured property of the insulation foam composite structure. While the ultimate properties (i.e., strength and elongation at

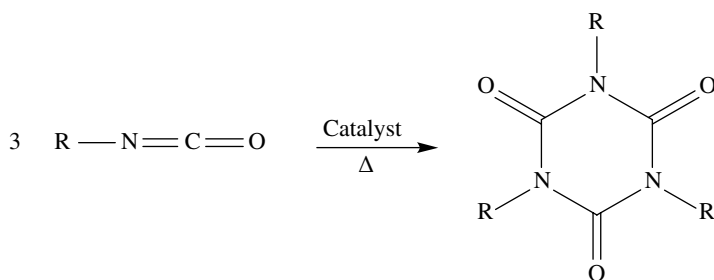


FIGURE 8.7 Trimerization of isocyanate functionality to form an isocyanurate ring. For rigid foams the R group would include additional unreacted isocyanate functionality capable of further reaction during polymerization.

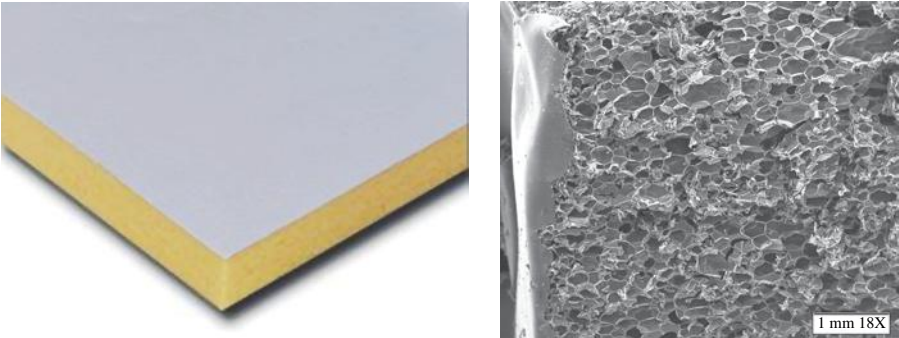


FIGURE 8.8 Photograph of an isocyanurate boardstock and scanning electron microscope image of the isocyanurate foam and the adhered aluminum film cover.

TABLE 8.1 Isocyanurate foam formulations and properties for making PIR insulation boardstock

Raw material	Formulation 1	Formulation 2
Polymeric MDI—average functionality=3.2 iso equiv wt=138	173	346
Cyclopentane/isopentane mixture (blowing agent)	20–26	27–33
Diol diester of phthalic anhydride with diethylene glycol (polyol) OH #227 functionality=2	100	100
Ester diol of tetrabromo phthalic anhydride/tris (1-chloro-2-propyl) phosphate flame retardant	4	32
Alkyl bromide (fire retardant)	0	16
Butylene oxide/ethylene oxide triblock surfactant	2.31	4
Water	0.46	0.75
Potassium acetate trimer catalyst	3–6	5–7
Isocyanate index	2.75	4.5
Foam properties		
Density w/o facer(lb/ft ³)	2.2	
Compressive strength (w/facer) (psi)	20–40 depending on orientation of test relative to board manufacture and direction	
% closed cell (5)	>95	
R-value/inch thickness depending on age of foam	6–8	
Flexural strength (psi)	20–30 (depending on composite thickness)	

Formulation 1 could be used in the slightly less-demanding wall insulation application, whereas Formulation 2 could be used in a roofing application. In practice, many contractors use the most flame resistant formula in all locations. The isocyanurate foam would normally be sandwiched between aluminum or polymer sheet and may have glass fiber matting within the composite structure.

break) are useful for predicting conditions for catastrophic structural failure, the low-strain properties are also useful for predicting the applicability of a structure for a specific application. As an isocyanurate sandwich board is a large composite structure, the flexural modulus can provide this kind of practical information [16]. The equation for the modulus of a bending beam (as measured by a three-point bend test) is given by Equation 8.1 where L is the beam length, b is the beam width, h is the beam height, and m is the slope of the linear elastic portion of the load deflection curve.

$$E_b = \frac{mL^3}{4bh^3} \quad (8.1)$$

In the case of an isocyanurate foam composite structure with the length and width of the structure held constant, the thickness of the insulation provides the main variable for controlling structural properties prior to failure. With the modulus varying as the inverse cubic power of thickness, it is seen that that foam thickness dominates the properties of the structure (Fig. 8.9) with small inclusions and flaws being minor perturbations.

Another property that the builder may try to influence is the overall insulation of a given structure. As Figure 8.10 shows, it is again the board thickness that most effects the expected energy conservation that can be designed in with the thickness–insulation relationship being linear. Isocyanurate foam (also called “iso” or “PIR” foam) is typically available in thicknesses from 0.5 to 2.375 in. They are made in plant manufacturing operations such as illustrated in (albeit simplified) Figure 8.11. The operation is complicated by the numerous processes

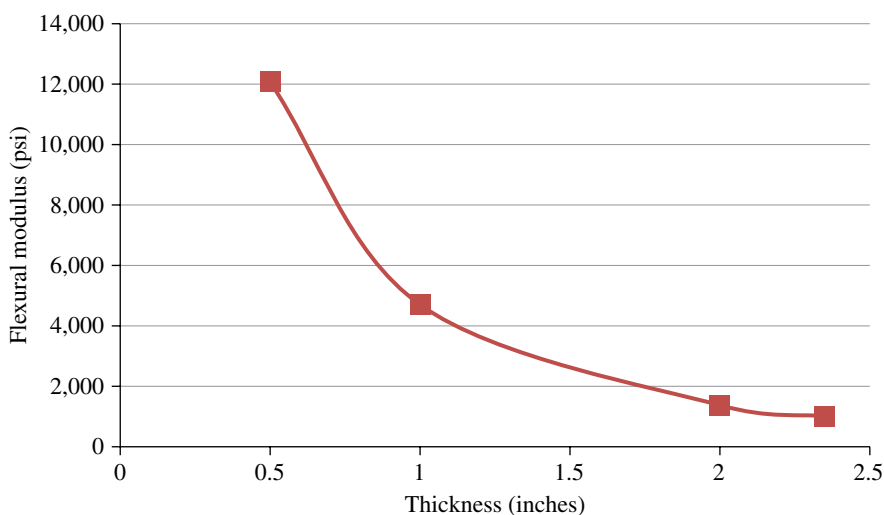


FIGURE 8.9 Measured flexural moduli of isocyanurate board properties using 6-in. long 2 in. wide samples with deflection rate or 0.5 in./min.

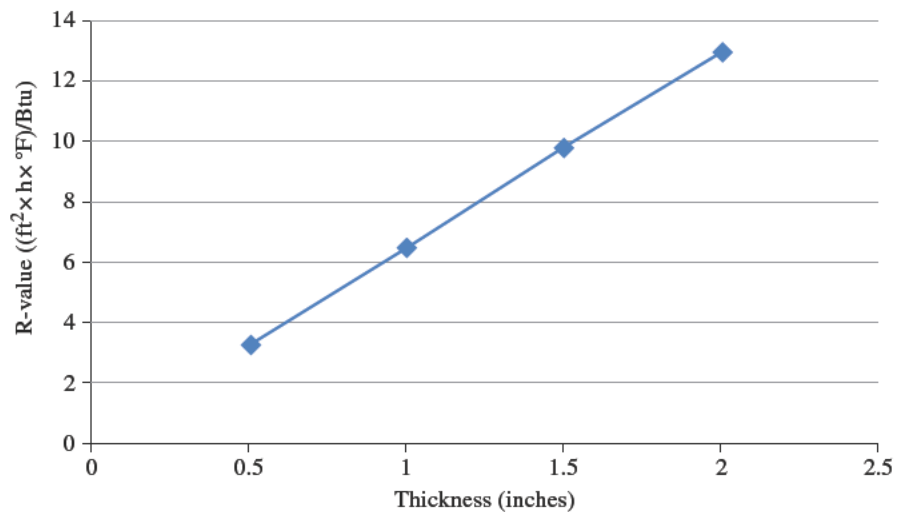


FIGURE 8.10 Measured *R*-value (ASTM C518) as a function of board thickness for formulations 1 and 2 of Table 8.1.

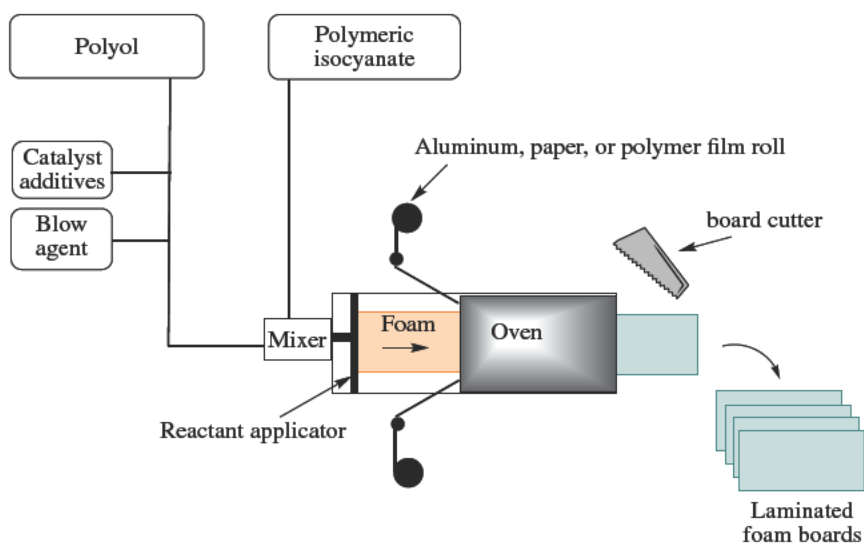


FIGURE 8.11 Schematic of the process for making isocyanurate boardstock. A third roll is sometimes installed with glass matt that gets laid directly into the foaming mass.

that are occurring simultaneously from the application of the reactants to the moving conveyor, the foam rise, the application of the laminating films, curing of the foam, development of adhesion to the film, and movement of the finished boards away from the process location. Economic efficiency requires the plant be used at high utilization and at high linear rates [17, 18]. Linear board rates of 60 m/min are possible;

however, this feat of engineering optimization can still be economically disadvantaged if the plant capacity is not run at or near maximum utilization, since there are other insulations, that although less effective, may still be price advantaged since isocyanurate insulation is the most expensive insulation product commonly available. Isocyanurate foam may be delivered a commercial advantage if the results of California State Assembly Bill 127, signed into law in September 2013, results in further tightening of building flammability standards.

8.2.1.2 Spray, Poured, and Froth Foams While isocyanurate boardstock rigid foams dominate the construction market, other modes of application find significant uses. The most common alternative application methods are called “pour-in-place” (PIP) and spray or froth spray. Both of these methods involve taking a formulated system of polyurethane building blocks, surfactants, catalysts, flame retardants, and so on, and performing the foaming at the construction site. Since the applicator is transporting a relatively dense liquid to then make very low-density foam, transportation costs are lower than with foam boardstock. Further, these modes can be used to apply foam over wide irregular areas in the case of spray, or to fill irregular cavities in the case of PIP.

Spray Foam Spray foams are used for the manufacture of insulated structures where coverage of large areas is needed, where insulation of complex shapes is required, and where coverage without joints or seams is required. The foam is applied through a mixing head/nozzle connected by hoses to two or more tanks containing the foam formulation. Since the foam must be applied quickly over wide areas, the formulation exits the application nozzle at a high velocity after high-pressure impingement mixing. Typical operating pressures are from 700 to 2000 psi. Because of the need to flexibly deliver insulation from a central tank system of feedstocks to walls and roofs, hose lengths can be as long as 300 ft or more. Like many liquid delivery nozzles, the end of the nozzle has a fixture to deliver a specific pattern that can be adjusted and substituted. Foam delivered by a spray method is usually qualified by a battery of standardized tests including those listed in Table 8.1. Specific qualifying spray foam tests are a reactivity profile, limiting oxygen index for flame ignition, flammability testing, smoke density testing, and trimer content (by FTIR; see Chapter 5). The procedure for developing a spray foam formulation is not simple and can be laborious and highly iterative. Achieving a system that meets all qualifying tests simultaneously is a challenge. The task is usually broken into four parts from which preliminary information and indications of performance can be gleaned prior to large-scale expensive flammability testing. This developmental procedure is summarized in Figure 8.12.

The rigid spray foam system is relatively simple in concept (see Fig. 8.13), but there are myriad details that are difficult to convey in a picture. As with all polyurethane systems, the quality of what is obtained depends on strict control of stoichiometry, which in the case of spray systems requires careful calibration, proportioning, and control of liquid pumping systems. Further, temperature and mixing conditions can likewise strongly influence foam properties. Last, it is the author’s experience that skill in handling the spray gun and choice of application pattern can also have a strong influence on insulation appearance and quality.

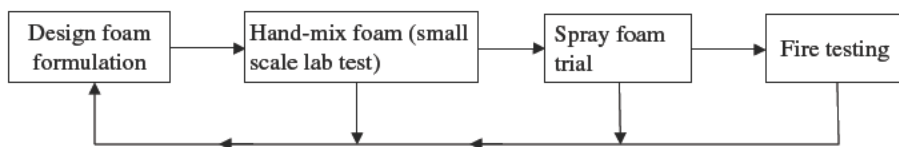


FIGURE 8.12 Typical process for developing a polyurethane spray foam formulation.

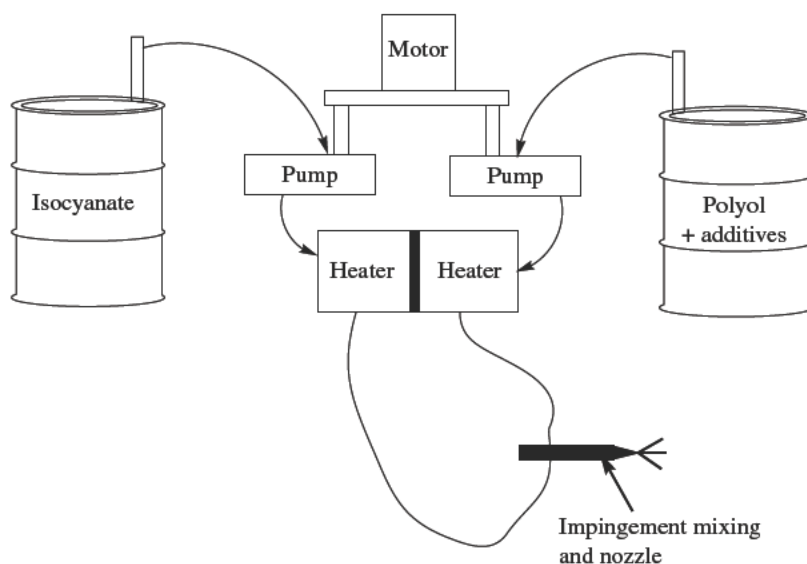


FIGURE 8.13 Schematic of the components for application of spray foam.

The formulation of foam will to some extent be dictated by application, building codes, and, increasingly, the building's insurer [19]. For many spray foams applied for roof insulation, the flammability inhibition must be very high (Class 1 determined by UL-94 test for flame spread and smoke generation), which can dictate the use of a relatively large amount of an optimized flame retardance/smoke inhibiting additive package. Table 8.2 provides example formulations for spray foam roofing applications and the measured properties and performance of these formulations.

A specific polyol initiated from a Mannich base [20] is specified in the formulations of Table 8.2. This is a unique polyol used almost exclusively in spray foam applications. It is unique in that it is (i) autocatalytic (see Chapter 2), (ii) has high functionality and low equivalent weight, and (iii) is aromatic. These attributes contribute to the requirements of spray foam technology by (i) speeding the reaction to enable fast rise at low cure temperatures, (ii) increase reaction rate and decrease gel times to improve reaction speeds and allow application to vertical surfaces, and (iii) contribution to the required flame retardance of the overall system. Figure 8.14 details the synthesis and structure of the polyol. The Mannich polyol most established for the spray foam application is the reaction product of nonyl phenol, formaldehyde, and diethanolamine. Manufacturers of Mannich polyols provide formulation

TABLE 8.2 Formulation for producing spray foams

Composition	Formulation 1	Formulation 2
Mannich base initiated three functional Equiv wt= 124 EO/PO mixed feed	16.1	46
PO/EO alkoxylated ethylene diamine (EO capped) Equiv wt= 74	6.4	15.5
Dimethyl terephthalate-initiated polyester polyol Equiv wt= 178	9.7	27.5
Glycerine	0.75	2.25
Trichloroethyl phosphate	4	11.5
Dibromoneopentylglycol	2	5.75
(1:4) Triethylene diamine/dimethylethanolamine	0.2	0.55
Silicone surfactant (DC 193)	0.35	1
Water	0.3	0.85
Blowing agent	10.5	30
Polymeric isocyanate 2.7 functional	51.8	30
Isocyanate index	1.14	1.2
Cream time (s)	13	10
Gel time (s)	27	25
Tack-free time	36	35
Density lbs/ft ³	1.5	1.93
Compressive strength (psi)		
Parallel to rise	30.4	29.2
Perpendicular to rise	13.6	21.9
<i>K</i> -factor (insulative value)	0.155	0.129
Dimensional stability 70 °C/95% humidity % volume change	1.6	1.6
ASTM E906 Burn test		
Smoke	2712	1927
Heat	303	406
% Weight loss	63	65

While the formulations are relatively different, the resulting foams only differ in some dimensions of performance showing that the formulation will be driven by the particular needs of the structure.

flexibility by varying the ratio of formaldehyde, ethanolamine, and alkoxylate to provide a specific equivalent weight and functionality.

Froth Foams Spray foams can be more efficient than foam boards in some applications due to the inefficiencies associated with transportation of bulky low-density materials. However, in some circumstances, spray foams can also be inefficient. For instance, spray foam applications tend to be large volume and large surface area. For applications where there are many relatively small areas to apply foam, a product has been established providing needed product convenience and cost effectiveness.

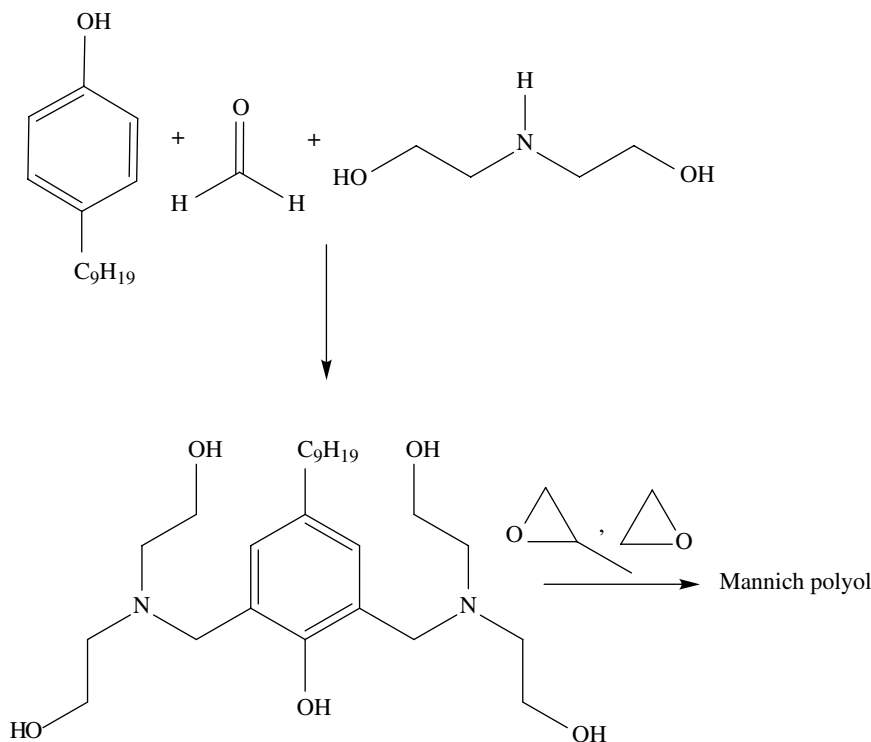


FIGURE 8.14 Process for production of Mannich polyols for use in spray foams.

Rather than the high pressure charging of materials in conventional spray foam combined in impingement mixing, the low-pressure application (called froth foam) product is charged at a relatively low pressure to a nozzle that has a static mixer contained within the nozzle handle [21]. The mixed polyurethane streams exit the nozzle in a relatively lower volume targeted spray that might allow insulation in a small crawl space ceiling, around a window frame, to a section of piping, to a small vessel, or other place for a spot application of insulation. The two component mixture is called froth foam due to the formulation components being charged to their vessels with insulating gas blowing agent, and often a pad of inert gas such as nitrogen. The tank pressure is in the range of hundreds of psi, and this gas pressure is the motive for the movement of materials from the tanks to the spray gun. Flows are controlled by valves to make sure the relative proportions of the two components are at the levels specified by the manufacturer. As indicated, both components of the froth foam system are under pressure. As the gas/polyurethane system flows into the relatively lower pressure environment of the nozzle handle, gas bubbles will begin to evolve from the flowing streams creating the froth. The frothing streams must mix in the static mixer within the handle. While the forming bubbles create some agitation in the liquid, their formation does not necessarily facilitate mixing. In fact, foams are notoriously poor as a mixing medium [22–24], and the static mixer and handle design

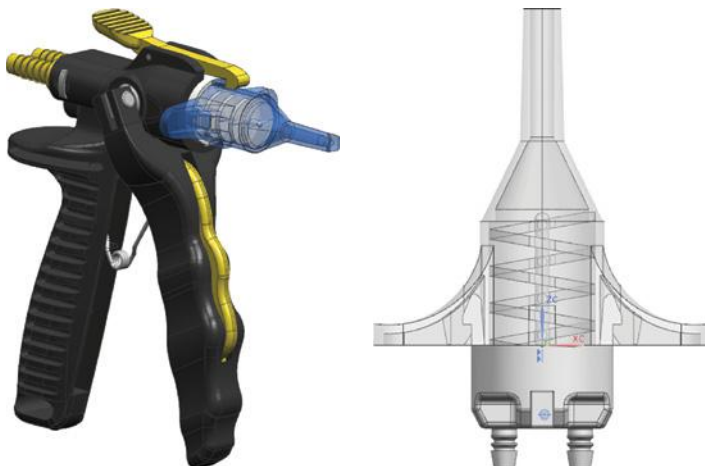


FIGURE 8.15 Drawings of (left) the external view of a froth foam gun and nozzle and (right) cutaway showing the froth chamber and static mixer. Image Courtesy of Peter Schultz Dow Chemical Company.



FIGURE 8.16 Form (left) of a purchased froth foam system and function (right) of a froth system in use. (See insert for color representation of the figure.)

is a highly engineered device and an object of highly competitive and fiercely protected intellectual property. In fact, more than the formulations comprising the foam, the nozzle and the ergonomics of the froth foam packaging are the most intensely patented aspects of this technology [25–29].

While the nozzle design is highly protected as a marketing asset, there are certain basic features that make up a typical nozzle. Such a generic nozzle is pictured in Figure 8.15 and the basic form of the product is shown in Figure 8.16. The contents of the froth foam formulation are unique in that the foam does not depend on the chemical reactions that occur to make the polyurethane reduce density. While some froth foam formulations will have water, the levels are small, usually on the order of 1% or less. Instead the froth foam depends on the expansion of the pressurizing gas

TABLE 8.3 Formulations for froth foam that might be use as a window sealant (Formulation 1) and as insulation foam for an attic space (Formulation 2)

Component	Formulation 1	Formulation 2
	Sealant applications	Insulation applications
Polyol side		
Polyester polyol terephthate ester of diethylene glycol equiv wt=178		17
Sucrose/glycerine-initiated 4.3 functional polyether polyol equiv wt=114	12	
Aromatic polyester polyol based on recycled PET, 2 functional 160 equiv wt	15	
Sucrose/glycerine-initiated PO polyol equiv wt=151 function=7		22.6
Sucrose/glycerine-initiated PO polyol equiv wt=155 function=4.5	14	
Trichloroethyl phosphate flame retardant	23	13.2
Triethyl phosphate flame retardant	2	3.6
Brominated diphenyl ether flame retardant		7
Dibutyl tin dimercaptide gel catalyst	0.7	1
Potassium octoate in DEG trimer catalyst	2	3.4
Penta methyl dipropylene triamine blow catalyst	0.7	
Silicone surfactant	2	1.1
Water	0.8	
1,1,1,2 Tetrafluoroethane blowing agent	19	19
1,1,1,3,3 Pentafluoropropane blowing agent	8.4	12
Isocyanate side		
Polymeric MDI 2.7 functional	92	92
1,1,1,2 Tetrafluoroethane blowing agent	7	7
Isocyanate stable silicone/polyether copolymer surfactant	1	1

and the blowing agent to create a porous structure. Some exemplary formulations are presented in Table 8.3, and a comparison of typical spray foam versus froth foam properties is given in Table 8.4.

PIP Foams PIP rigid construction foams fill a particular application space that other less-expensive techniques cannot be modified to fill. PIP is a discontinuous foam production process that places foams in complex cavities less expensively than low-volume froth foam techniques, and much less expensively than highly capital-intensive continuous techniques [30, 31]. Like froth foams, the components are taken to the application site, mixed, and poured or sprayed into cavities. The polyurethane building block chemicals then foam to fill the cavities. The requirements of this process are unique but can overlap the other methods depending on the details of “the pour.” One distinguishing feature of PIP is that the foaming and cure are somewhat slower than spray and froth applied foams since the foam must be able to flow into all the cavities

TABLE 8.4 Comparison of typical properties of high-pressure spray foam and froth foams

Property	Spray foam (Class I)	Froth
Gel time at 75 °F (s)	8–10	8–10
Rise time at 75 °F (s)	12–15	40
Aged <i>R</i> value/in (ft ² -h-°F/BTU)	6.2	5.4
Aged 90 days at 140 °F		
Water vapor permeability ASTM E96 (perm-in)	3	<5
Compressive strength ASTM D1621 (lb/in ²)	25	>15
Closed cell content ASTM D 6226 (%)	90	90
Dimensional stability ASTM D2126 (% linear change)	9	<12
Aged 7 days at 158 °F 97% relative humidity		
Surface burning characteristic ASTM E84	Class 1	Class B (at 2 in. thick)

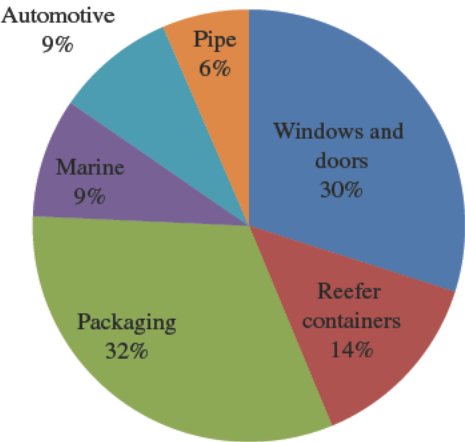


FIGURE 8.17 Pour-in-place application segments (nonappliance).

and irregularities. Foam thickness in PIP applications can be significantly larger than other rigid foam applications. The applications PIP applications methods find their largest uses in are shown in Figure 8.17.

The details of the cavity dictate the processing technique. The cavity filling technique must effect uniform distribution of the mixed and reacting polyurethane, optimize flow to all parts of the cavity, allow for displaced air to escape, eliminate entrapped air, minimize void formation, and minimize cell orientation (anisotropy) [32]. Like high-pressure spray techniques, the two components must be mixed, and this is usually achieved using impingement techniques such as occur in spray polyurethane foam operations [33–35]. However, unlike spray foams, PIP exits the nozzle with a relatively slow forward velocity and with laminar flow. In addition, unlike spray foam, PIP operates with a controlled, usually programmed time or volume-controlled shot size. The foam is

then injected into the cavity using procedures optimized for the particular shape. An alternative technique uses a lance withdrawal approach. In this method, a hollow wand directs the polyurethane components into the cavity which will be moved about the volume and withdrawn as the components are deposited. This technique minimizes the flow requirements of the dispensed foaming mixture and is useful for narrow and long cavities of moderate-to-lower volumes.

As mentioned earlier, relative to spray techniques, a discontinuous technique such as PIP requires slower reactivity. Relative to spray application that must gel in less than 10 s, PIP foams gel in 90–120 s for larger cavities, and 30–50 s for smaller cavities such as entry doors. The ideal foam insertion initiates volume expansion after completion of liquid injection to minimize pouring (and concomitant partial distortion and collapse) into a rising foam. The reacting foam should gel shortly after rise to minimize cell anisotropy (stretching in the rise direction) and resulting weakening of the foam. Last, the PIP foam must fill the space intended, but not deform the object containing it. For example, when poured into a window frame, a hollow entry door, a reefer container, or a boat's hull cavity, it must not deform the object containing it due to overexpansion of the foam by overfilling, or to overpressure of the blowing gas. Such perfect performance is not usually realized but is approached by the appropriate formulation choices. Table 8.5 provides example formulations of PIP foams for different uses. The flame-retardant requirements are often less for PIP applications than for wall and roof insulations that have a larger surface, whereas PIP foams are encased in a containing envelope that also protects the foam from an initial ignition source [36].

Water-blown PIP technologies exist in the market place, and in some cases can have a price advantage over new generation fluorocarbon-blowing agent formulations due to the high prices of blowing agents. Water-blown PIP can be disadvantaged by having significantly longer cure times, higher densities, and higher K values (lower R values—poorer insulation properties). In addition, they can often have significantly higher viscosity that complicates the efficiency of mixing and nozzle delivery. Of course, blowing agent formulations along with being more expensive also require the use of pressurized tanks to maintain the system sides in a liquid state.

8.2.2 Rigid Construction Foam Market Segments

Reliable data on the segment volumes are difficult to obtain with a wide range of values available in market surveys. All surveys find that the majority of polyurethane rigid foams in the construction market are isocyanurate with volume percentage ranging from approximately 50 to 75%. Available data are incomplete, but a rough average is presented in Figure 8.18, showing historical context and consistency over time and the role of geography on application preferences.

The construction rigid foam market is primarily segmented on the structural part being insulated. This segmentation breaks into roofing, walls, tanks and pipes, refrigerated buildings, and metal or fiberglass doors. The breakdown in utilization is provided in Figure 8.19. While the details of this distribution change slightly over time, the percentage breakdown given in the figure has been relatively stable for 20 years. Door insulation is well under 1% of the total rigid foam usage and is neglected in this figure to simplify the representation

TABLE 8.5 Formulations and properties for three pour-in-place applications

Component	Water blown	Marine formulation	Door cavity formulation
Iso side			
Polymeric MDI, 2.7 functional Iso equiv wt = 134 g/equiv	163.5	136.5	136.3
1,1,1,2 Tetrafluoroethane blowing agent		0.83	0.83
Isocyanate stable silicone/polyether copolymer surfactant		4.7	5.25
Polyol side			
Aromatic phthalate polyester polyol 2.3 functional OH equiv wt = 211 g/equiv			54
Mixture of sucrose/glycerine and glycerine initiated polyols function = 3.6 OH equiv wt = 167	100		
Sucrose/glycerine-initiated function = 4.5 equiv wt = 155		50	27
<i>o</i> -Toluene diamine-initiated 4 function equiv wt = 143		50	
Glycerine-initiated PO polyol functionality function = 3 OH equiv wt = 85			5.5
Mix of sucrose/glycerine and sucrose-initiated PO/EO-capped polyol Function = 7 OH equiv wt = 200			13.5
Tris (2-chloropropyl)phosphate flame retardant	5	18	17
Bis aliphatic epoxy			1.4
Dimethylethanolamine reactive catalyst	0.1		
Pentamethyl diethylene triamine catalyst		0.1	
<i>N,N</i> dimethyl cyclohexyl amine		0.06	
70/30 1,2 Dimethylimidazole in DEG			0.25
Silicone surfactant, i.e., DABCO DC 193		1.9	2.1
EO ₃₈ /BO ₄₆ /EO ₃₈ triblock polyol surfactant	5		
Water	4		
1,1,1,2 Tetrafluoroethane blowing agent		22	18

Property	Water blown	Marine formulation	Door cavity formulation
Gel time (s)	365	150	220
Tack-free time (s)	731	237	418
Density (lbs/ft ³)	2.3	1.6	1.8
Initial <i>K</i> -factor	0.21	0.16	0.16

The water-blown formulation would be considered for applications where insulation is not a primary consideration as in automotive support members.

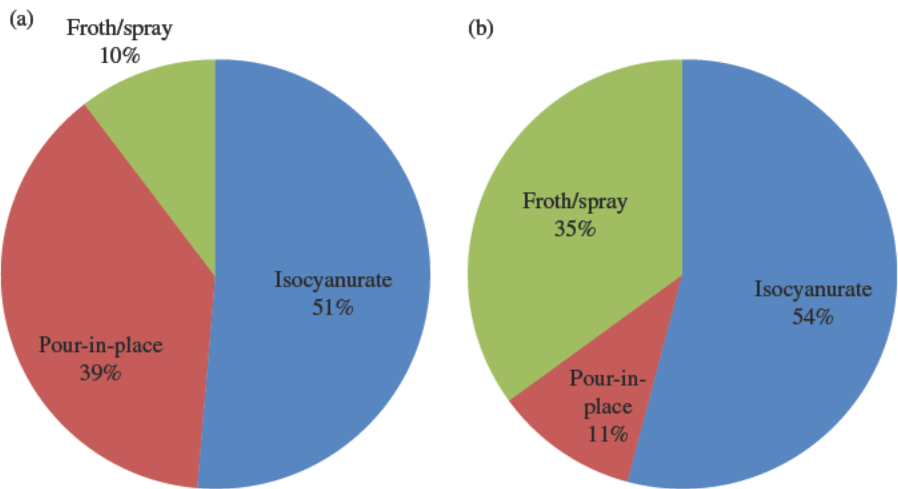


FIGURE 8.18 Global segmentation of rigid construction foams (a) globally in 2002 and (b) the United States in 2012. Geographical differences may reflect capital investment avoidance in spray systems in some geographies.

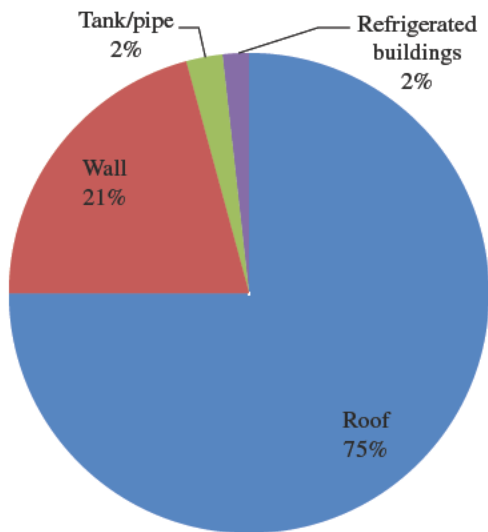


FIGURE 8.19 Segmentation of the polyurethane rigid foams for construction market by volume consumed in 2012.

With roofing and wall insulation representing virtually all of the construction market for polyurethane rigid foams, the regulatory standards for performance are critical to successful commercial positioning. Table 8.6 is a list of relevant tests for determining the suitability, performance, and risk associated with insulation systems such as polyisocyanurate systems. Individual states and countries may require

TABLE 8.6 List of standard tests and descriptions relevant to the polyurethane rigid foam construction applications

Test	Standard description
ASTM C1289-13	Standard specification for faced rigid polyisocyanurate thermal insulation board including general industry requirements for materials and performance. Only for faced boards
ASTM C591-12	Standard specification for unfaced preformed rigid cellular polyisocyanurate thermal insulation including general requirements, specifications, and dimensions for unfaced boards only.
ASTM C1303-12	Standard test method for predicting long-term thermal resistance of closed-cell foam insulation. Only applicable to unfaced or permeably faced insulation. Uses accelerated aging conditions.
ASTM E1730-09	Standard specification for rigid foam for use in structural sandwich panel cores. Structural testing of composite structural insulation panels including impact, flame resistance, thermal conductivity, compressive, tensile, and shear strength.
ASTM E84-13	Standard test method for surface burning characteristics of building materials. Determines the relative flame spread and smoke density generation produced. Uses long (24 ft) and wide (20 in.) specimens.
ASTM E662-13	Standard test method for specific optical density of smoke generated by solid materials. Quantification of the attenuation of a light beam by smoke in a closed chamber.
ASTM E1465-08	Standard practice for radon control option for the design and construction of new low-rise residential buildings. Primarily, a piping system for detouring radon from penetrating the structure. Piping may need insulation and radon build-up made more severe by improved insulation.
ASTM E1678-10	Standard test method for measuring smoke toxicity for use in fire hazard analysis. Collection and analysis of smoke followed by animal testing for LC_{50} for exposure to smoke.
ASTM E906	Also called “the OSU burn test” standard methods for heat and visible smoke release rates for materials and products
DIN 4102-1 B3	German standard fire test to building materials (sic) standard defines fire behavior classes and specifies requirements and test methods for each class. Urethane based materials generally fall under B3 classification suggesting intrinsic flammability
ISO 5660	International Organization for Standardization. Reaction-to-fire test heat release, smoke production, and mass loss rate (cone calorimeter method). Measure time to ignition and heat release rate based on oxygen consumption in a calibrated gas flow.
UL-94	Underwriters Laboratory test for plastics flammability using small specimens (5 in. × 0.5 in.) measures tendency of a material to self-extinguish or spread a flame one ignition occurs.
ASHRAE 90.1	Energy standard for building except low-rise residential buildings. States apply the standards differently over the range of building purposes.
BS EN 13823	British standard for materials of construction, relatively small scale, measures heat output, and smoke generation in a corner geometry.

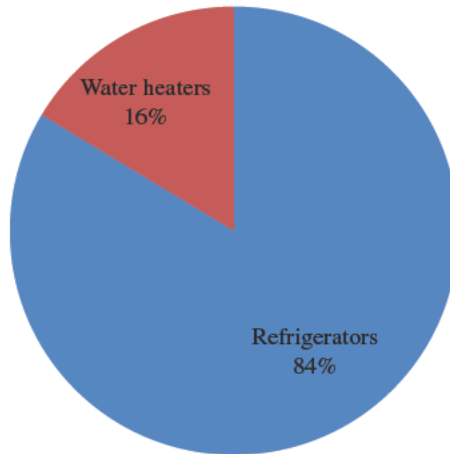


FIGURE 8.20 Percentage consumption of polyurethane rigid foams for appliance insulation.

additional testing or performance to meet local requirements. Along with standard testing methods issued by national organizations such as ASTM, and European and Asian testing organizations, there also exist trade organizations such as American Society of Heating, Refrigerating and Air-Conditioning Engineers (ASHRAE) promulgating standards. Aside from characterization of the foam structure, their standards apply to the overall performance of the structure that the foam insulation must be a part of meeting targets [37].

8.2.3 Appliance Foams

Appliance foams have similarities to PIP foams in that they are used to fill a cavity and that they must not deform the cavity during foam rise due to expansion pressures or during contraction as the foam cools. The majority of polyurethane appliance foams are used for refrigeration including refrigerators, freezers, coolers, refrigerated trucks, and railcars [38]. Another category is used for water heaters. Figure 8.20 breaks down the approximate volume ratios that occupy these two market segments. While there is a continuing demand for consumer appliances, the aggregate demand follows the construction market and particularly new home construction. Commercial trends in these markets relate to consumers obtaining second refrigerators and freezers, and growing use of refrigerated vending machines and display cases [39].

The typical polyurethane components of appliance foams are also similar to PIP foams with the notable exception that appliance foams are expected to provide little in the way of flame retardance relative to construction foams, or even flexible foams used in furniture. What they are expected to provide is (i) the ability to rise and cure rapidly with no deformation of the refrigerator or water heater cabinet, and

(ii) a high degree of insulation performance. Along with energy savings to the customer, highly efficient insulation allows the manufacturer to specify a smaller, less-expensive compressor for refrigeration to maintain a larger capacity. Optimum design can also help make up for poorer insulation efficiency arising from the use of environment-friendly, if less efficient, blowing agent/insulating gases. A discussion of insulating gases comes later in this chapter. Table 8.7 provides example appliance foam formulations.

The data given in Table 8.7 are actual for the foam formulations given, but the properties should be viewed as representative and illustrative of the fact that blowing agents are a major component of the formulation, and can have a major influence on the formulation and the properties. Further, different compartments of an insulating unit (i.e. the freezer cabinet vs. the freezer door) may require more or less efficiency, and the manufacturer may inject more than one foam formulation to optimize performance and price.

Table 8.8 provides a general guide to property requirements for this segment. Properties achieved with any particular formulation are variable and will depend greatly on numerous process specifics including the details of the injection, the shape of the mold to be filled, the ambient temperature, even the geographic elevation of the manufacturer making the insulation foam. While the properties may vary, the general trend in formulation optimization is indicated in Table 8.8 as designers continuously try to enhance foam efficiency along all performance dimensions.

While there are ASTM tests for measurement of thermal insulation panel performance such as ASTM C518, in the case of polyurethane rigid foams for appliance applications, the manufacturer will often rely on internal tests of performance. Rather than a screening test on the foam component, the test will incorporate the entire molded and foamed cabinet. This makes sense since energy leakage from, or into, a container such as a refrigerator may depend on the envelope materials and the overall design of the cabinet. Many of these tests are performed to conform to regulatory agency mandates requiring explicit evaluation and communication with consumers about expected energy consumption. An example of such protocols is the US Department of Energy “*Uniform Test Method for Measuring the Energy Consumption of Electric Refrigerators and Electric Refrigerator-Freezers*” 10 CFR Appendix A1 to subpart B of part 430. A screening test for this battery of standardized tests and conditions is the test outlined by the Association of Home Appliance Manufacturers (AHAMs) test referred to as the “reverse heat leakage” (RHL) test. The RHL test is performed on a complete cabinet without an installed compressor. A light bulb and energizing circuit is placed inside the insulated cabinet that is then placed in a cold room (Fig. 8.21). The light bulb is energized and the amount of energy required maintaining the interior at an elevated temperature is recorded. While still a bit involved and requiring a high level of control, this is a relatively low-cost method to screen the thermal efficiency of a foam-insulated appliance. The overall refrigerator conductance (R_c) is calculated from this experiment using Equation 8.2, where the temperature is usually an average of several measurements [40].

TABLE 8.7 Formulations and properties for use in appliance insulation applications

Formulation 1 components	Formulation 1 (wt%)	Formulation 2	Formulation 2 (wt%)
Sucrose/glycerine-initiated function = 5.2 Equiv wt = 108 g/equiv all PO	33.8	Propoxylated sorbitol function = 6 equiv wt = 116 g/equiv	63
Propoxylated ethylene diamine function = 4 equiv wt = 87	10.35	Propoxylated glycerine function = 3 equiv wt = 360 g/equiv	25
Toluene diamine-initiated function = 4 equiv wt = 121	7	Propoxylated ethylene diamine function = 4 equiv. wt = 112 g/equiv	5
Aromatic polyester polol phthalic anhydride with diethylene glycol function = 2 equiv wt = 185	17.2	Water	2.5
Pentamethyldiethylene triamine (blow catalyst)	0.55	2,4,6 tris-dimethylamino phenol (delayed trimer catalyst)	0.7
<i>N,N</i> dimethylcyclohexyl amine (gel- balanced catalyst)	0.8	Pentamethyldiethylene triamine (blow catalyst)	1.3
Potassium acetate in ethylene glycol (trimer catalyst)	0.2	Potassium octoate in diethylene glycol	0.1
2,4,6 Tris-dimethylamino phenol (delayed trimer catalyst)	0.8	Polyether modified polysiloxane copolymer (surfactant)	2.5
Polyether modified polysiloxane copolymer (surfactant)	1.8	85/15% Cyclopentane/isopentane (blowing agent)	14.5
Water (blowing agent and chain extender)	1		
1,1-Dichloro-1-fluoroethane (blowing agent)	26.5		

Polymeric MDI 2.7 functional equiv wt = 134 g/equiv (iso index = 1.3)	118	Polymeric MDI 2.7 functional equiv wt = 134 g/equiv (iso index = 1.3)	146
Mol wt per crosslink			348
Cream time (s)	6	Cream time (s)	4
Gelation time (s)	39	Gelation time (s)	47
Tack free time (s)	45	Tack free time (s)	60
Density(lbs/ft ³)	1.9	Density(lbs/ft ³)	2.0
K (25 °C,(BTU in)/(h/ft ² °F)	0.12	K (25 °C,(BTU in)/(h/ft ² °F)	0.16
Compressive strength, x-, y-axis (psi)	22.5, 32	Compressive strength, x-axis (psi)	19, 34

Formulation 1 employs a chlorofluorocarbon blowing agent and has superior insulation properties, while the other uses a hydrocarbon blowing agent.

TABLE 8.8 Typical range of rigid polyurethane foams for appliances and the direction foam designers are trying to improve their foams in that dimension

Property	Units	Value range	Direction of improvement
Thermal conductivity	BTU in)/(h/ft ² °F)	0.12–0.16	↓
Density	lbs/ft ³	1.8–2.2	↓
Compressive strength	psi	>16	↑
Demold time	s	190–240	↓
Post demold expansion	%	0–3	↓

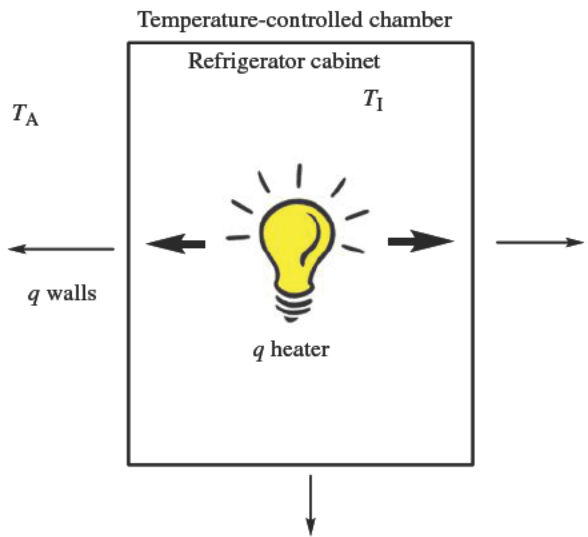


FIGURE 8.21 Illustration of the concepts in a reverse heat loss test for refrigeration insulation efficiency.

$$R_c = \frac{q_{\text{heater}}}{T_I - T_A} = \frac{q_{\text{walls}}}{T_I - T_A} \tag{8.2}$$

The reverse heat loss measurement correlates very strongly with the thermal conductivity of the blowing agent insulating gas employed for making the rigid foam as shown for a controlled data set (Fig. 8.22) [41].

Figure 8.22 shows the importance of the blowing agent on the insulation performance and on the manufacturer’s ability to meet regulator and customer expectation. In fact, as will be shown later, blowing agent technology and associated

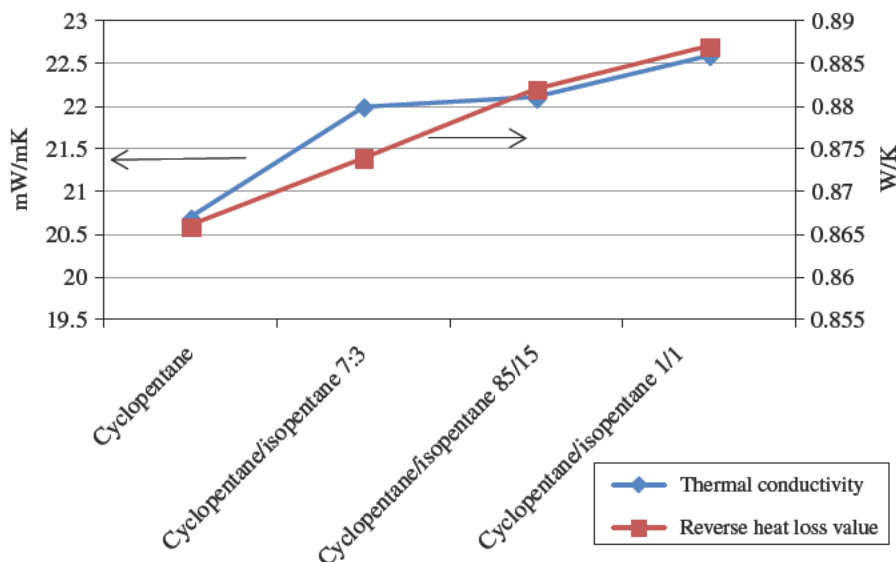


FIGURE 8.22 Relationship between measured blowing agent thermal conductivity and the results for reverse heat loss test using foams blown with the same blowing agents.

formulation adjustments make up the field of most intense patent activity for the large polyurethane building block providers despite the fact that none of them is a blowing agent manufacturer.

8.3 BLOWING AGENTS AND INSULATION FUNDAMENTALS

8.3.1 Blowing Agents

As Figure 8.22 shows, the manufacturer and consumer have a significant stake in the choice of blowing agent that is made. The manufacturer must meet regulatory, cost, and quality requirements in production. At the same time, the economics of ownership are affected greatly by insulation efficiency [42–44]. In addition to these prosaic considerations, there is the recognized influence blowing agents can have on the global environment. There is particularly recognition that certain blowing agents that were previously ubiquitous are capable of depleting ozone present in the upper atmosphere [45–47]. While ozone in the lower atmosphere is regarded as a pollutant, in the upper atmosphere (stratosphere) ozone serves as a necessary filter on high energy UV-B radiation. In 1973, Chemists F. Rowland and M. Molina showed that the high vapor pressure and stability of chlorofluorocarbons, commonly used blowing agents and propellants, could be dissociated by UV radiation, releasing a chlorine atom, that proceeded to breakdown ozone [48]. The removal of ozone from the upper atmosphere, responsible for filtering of UV radiation would result in a greater flux of UV radiation at the Earth's surface increasing the potential for skin cancer and cell damage to living things.

TABLE 8.9 Properties of rigid polyurethane foam blowing agents, several of which are banned or scheduled for phase out

Blowing agent	Chemical Formula	Molecular weight g/mol	Boiling point (°C)	K-factor (mW/mK)	ODP	GWP
CFC-11	Cl ₃ CF	137.5	23.8	7.9	1.0	3400
HCFC-123	C ₂ HCl ₂ F ₃	152.9	27.9	9.5	0.02	93
HCFC-141b	CH ₃ -CCl ₂ F	116.9	32	8.7	0.11	610
HCFC-142b	CH ₃ -CF ₂ Cl	100.5	-9.8	11.6	0.065	1600
HCFC-134a	C ₂ H ₂ F ₄	102	-26.5	14.5	0	1320
HFC-245fa	CHF ₂ CH ₂ CF ₃	134	15	12.4	0	1020
HFC-365mfc	C ₄ H ₅ F ₅ (1,1,1,3,3,3 pentafluorobutane)	148	40	10.5	0	782
FEA-1100	1,1,1,3,3,3 hexafluoro 2-3 butene	164	33	10.7	0	9
Carbon dioxide	CO ₂	44	-78	16.5	0	1.0
Air	N ₂ /O ₂	28.8	-192	29	0	0
<i>n</i> -pentane	C ₅ H ₁₂	72	36	14.8	0	20
<i>Iso</i> -pentane	C ₅ H ₁₂	72	28	14	0	11
Cyclopentane	C ₅ H ₁₀	70	50	12.9	0	10

GWP, relative global warming potential; ODP, relative ozone depletion potential.

In 1987, an international treaty was signed [49] to protect the ozone layer by phasing out production and use of chemicals capable of depleting stratospheric ozone. Since then, it has undergone numerous revisions and updates and has been ratified and upheld by almost all nations. Among the revisions, the protocols have recognized that in addition to their potential for ozone depletion (ODP), chemicals useful for blowing agents can be scrutinized for their contributions to global warming potential (GWP) with several blowing agents showing orders of magnitude more GWP than CO₂. Recent attention has also focused on the atmospheric lifetime of blowing agents. Since the effect of this treaty and its revisions has a major effect on the industrial practice of making polyurethane foams for insulation, it is of major interest to practitioners of polyurethane science.

Table 8.9 is a partial compendium of blowing agents that have been used for preparation of rigid polyurethane insulation foams. Other blowing agents have been explored and have been mixed in attempts to obtain synergistic effects or dilute the different negative issues one agent has without harming the positive attributes that may come in the pairing.

8.3.2 Blowing Agent Phase-Out Schedule

Government regulation drives a significant amount of technology innovation for companies involved with rigid polyurethanes. As will be discussed in Section 8.4, insulation efficiency requirements and blowing agent restrictions are inextricable.

TABLE 8.10 Promulgation of regulations for blowing agents previously used for polyurethane rigid foams

Date	US regulation
January 1, 1994	Banned production of bromochlorodifluoromethane (Halon 1211), bromotrifluoromethane (Halon 1301) and dibromotetrafluoroethane (Halon 2402) (and isomers)
January 1, 1996	Production of chlorofluorocarbons banned except for very critical applications such as emergency inhalers and research.
January 1, 2004	Restricted of 1,1,-dichloro-1-fluoroethane (HCF-141b) by 35%, 75% reduction by 2010 and total phase out by 2040. With alternatives available, the United States EPA <i>does not</i> consider it an acceptable substitute for chlorofluorocarbons in PU foam blowing.
Date	European regulation
January 1, 2005	Phase out of 1,1,dichloro-1-fluoroethane and other hydrochlorofluorocarbons. Different nations within the European Union adopted different schedules (often faster). Allowing for only very limited production and consumption after January 1, 2010 and for some banned after 2020 and others banned after 2030.
January 1, 2012	Broad regulation affecting hydrofluorocarbons and perfluorocarbons proposed including HFC 245, HFC 134a and HFC 365mfc. This is a tightening of regulations previously proposed in 2006.
Date	Japanese regulations
January 1, 1994	Phase out of bromochlorodifluoromethane (Halon 1211), bromotrifluoromethane (Halon 1301) and dibromotetrafluoroethane (Halon 2402) (and isomers)
January 1, 1996	All CFC phased out
1996	Began phase out of HCFC consumption with gradual phase out to 65% of 2003 consumption by 2009, 35% of 2003 consumption by 2014, and 10% of 2003 consumption by 2019 and total phase out by 2020.

Approximately 75% of the insulative potential of a foam depends on the foam structure and the properties of the gas within the closed cells, both of which the blowing agent has strongly causative relationships to. Regulations governing industrial use of blowing agents are particularly relevant to polyurethane technology because they not only govern current use but also future use, since whole classes are designated for banning in future years [50]. Table 8.10 is a compendium of relevant historical and future restrictions. Future restrictions will provoke a significant amount of reformulation of polyurethane systems along with development of new classes

TABLE 8.11 Restricted blowing agents and potential substitutes for polyurethane rigid foam production

Accepted blowing agent	Regulated or restricted blowing agent
HCFC-123 (2,2 dichloro 1,1,1 trifluoroethane)	CFC-11
HFC-134a (1,1,1,2 tetrafluoroethane)	CFC-11, HCFCs
HFC-152a (1,1, difluoroethane)	CFC-11, HCFCs
HFC-245fa (1,1,1,3,3 pentafluoropropane)	CFC-11, HCFCs
HCFC-141b/HCFC-123 Blends	CFC-11
Formic Acid (HCOOH) a latent producer of CO and CO ₂	CFC-11, HCFCs
Carbon Dioxide	CFC-11, HCFCs
Water	HCFCs
Pentane isomers (C ₅ H ₁₂ and C ₅ H ₁₀)	HCFCs
Methyl formate (HCOOCH ₃)	CFCs, HCFCs
HFO-1234ze (1,3,3,3 tetrafluoropropene)	CFCs, HCFCs
HFC-365mfc (1,1,1,3,3 tetrafluorobutane)	HCFC-141b; HCFC-22, HCFC-142b, and blends thereof
Formacel® TI (proprietary blend)	HCFC-22, HCFC-142b
Trans-1-chloro-3,3,3-trifluoroprop-1-ene	CFC-11, HCFC-141b

Some of the options are suggested for use only in combination with other agents.

of blowing agent. Along with insulation potential, a blowing agent must also possess sufficient solubility in foam formulations to result in low-density foam, must be acceptable from an environmental health and safety standpoint, must have acceptable flammability characteristics, and must be compatible with equipment and other formulation additives. The dates listed are not universally implemented on the same time schedule, but given the commercial importance of the US and European markets for polyurethane rigid foams, they certainly are milestones for industrial use of blowing agents. In fact, some countries have implemented restrictions on accelerated time schedules.

An alternative view is to look at what blowing agents are allowed and the typical regulated blowing agent it can replace (Table 8.11).

8.4 INSULATION FUNDAMENTALS

The worldwide acceptance and use of polyurethane foams for insulation applications focuses competition and innovation toward making the best product at the best price. As research organizations mobilize to improve the use of insulation materials, it is natural to focus on those aspects that can exhibit the most improvement. Analyzing the performance of an insulation foam means quantifying the physical contributions of each structural and chemical feature for its influence on thermal conduction. Thermal conductivity or the “K-factor” is the proportionality

constant between the heat flow per unit area (q) and the thermal gradient through the substance in question (Eq. 8.3) [51].

$$q = \frac{\partial Q / \partial T}{A} = K(T_1 - T_2) \quad (8.3)$$

The lower the thermal conductivity of a substance (in our case a polyurethane foam), the lower the heat flow rate per unit area across the sample for a given temperature gradient, and the better its performance as an insulation material. Commercial insulation materials are normally identified by their “ R ” value which is product specific based on its thickness L , and is related to q by Equation 8.4 [52]:

$$R = \frac{L}{K} \quad (8.4)$$

$$q = \frac{T_1 - T_2}{R}$$

The units of K in the SI system are (watts/(meter $\times$ Kelvin)) and also often expressed in terms of imperial units ((BTU $\times$ in.)/(h $\times$ ft² $\times$ °F)) where a British thermal unit (BTU) is the energy to raise a pound of water by 1 °F or about 1055 J.

When a polyurethane foam is applied as an insulation, it displaces air and substitutes the gas entrapped in the foam (95% of the substitution by volume) and the polyurethane material. The foam walls and windows serve to scatter and impede radiative conduction of heat. At the same time, the polyurethane acts as a conduction path for heat transport through the material. Not counting the influence of one path on another (an interaction term) the k -factor for a polyurethane foam is the sum of three conduction terms (Eq. 8.5):

$$K_{\text{foam}} = K_{\text{solid}} + K_{\text{gas}} + K_{\text{radiative}} \quad (8.5)$$

Where K_{solid} is the solid conduction component of the foam K -factor, K_{gas} is the gas conduction component of the foam K -factor, and $K_{\text{radiative}}$ is the radiative component of the foam K -factor [53–55].

Given the very low densities of rigid foams (typically >95% pore volume), the solid component is usually ignored in a first approximation but can account for about 10% of the total heat transfer across a foam [56]. The radiative component is that associated with temperature difference and not gradient. It is commonly associated with black-body emission and is thus a function of foam thickness and density, but not the material itself. This factor can account for about 15% of the heat transfer across a foam [57]. The remaining heat conduction is associated with that due to transfer through the gas phase. Consequently, both the solid and radiative components are minor contributors to the overall thermal foam conduction and even significant improvements in their K -factor contribution would be minor in overall effect. Accordingly, the gas conduction component has become the focus of almost all attempts to improve the insulation properties of polyurethane rigid foams [58–60].

A simple first-order expression for the thermal conductivity of gases is obtained from kinetic molecular theory (Eq. 8.6) [61]:

$$K_{\text{gas}} = \frac{f}{2\pi b^2} \left[\frac{k_B^3 N_o T}{\pi m_o} \right]^{1/2} \quad (8.6)$$

Where T is absolute temperature, m_o is the molecular weight of the gas molecules, b is the molecular diameter, f is the number of degrees of freedom per molecule, N_o is Avogadro's number ($6.023 \times 10^{23} \text{ mol}^{-1}$) and k_B is Boltzmann's constant ($1.38 \times 10^{-23} \text{ J/K}$). This equation predicts that the thermal conductivity of gases is independent of pressure, proportional to the square root of the system temperature, and has inverse proportionality to molecular mass. This equation is confirmed by experiment at ambient temperatures and pressures [62]. Refinements of Equation 8.6 have been developed by taking into account the potential for energy transfer between molecular vibration or rotational modes into translational energy [63]. Equation 8.6 can be expressed in terms of gas viscosity ν , density ρ , pressure P , molecular speed u , mean free path l_o , specific heat c_o , and the gas constant R (8.314 J/(molK)) as Equation 8.7.

$$K_{\text{gas}} = \frac{1}{2} f \rho u l_o \frac{R}{2m_o} \quad (8.7)$$

Terms in Equation 8.7 can be calculated using the relationships in Equation 8.8.

$$\begin{aligned} \rho &= \frac{Pm_o}{RT} \\ u &= \left[\frac{8RT}{\pi m_o} \right]^{1/2} \\ I_o &= \frac{k_B T}{\sqrt{2} \pi b^2 P} \\ \nu &= \frac{1}{2} \rho u I_o \quad \text{or by substitution} \\ &= \frac{1}{\pi b^2} \left[\frac{k_B m_o T}{\pi N_o} \right]^{1/2} \end{aligned} \quad (8.8)$$

For air the mean free path (in micrometers) is $2.24 \times 10^{-4} T(K)/P(\text{atm})$ or about $0.07 \mu\text{m}$ at room temperature.

Rigid foam designers have employed gas mixtures as a means to improve overall insulation cost and performance. The thermal conductivity (k -factor) of a mixture of gases at normal temperatures and pressures has been described by the Riblett equation (8.9) [63]. Variations and refinements have been proposed to take account of observed deviations from Equation 8.9.

$$k_{\text{gas}} = \frac{\sum P_i m_i^{1/3} k_i}{\sum P_i m_i^{1/3}} \quad (8.9)$$

While mixing gases has been one route to improve the gas conductivity of polyurethane insulation foam, another route has been to take advantage of the Knudsen effect [64–67]. The Knudsen effect takes into account the fact that thermal transport by the gas phase assumes that the mean free path between molecular collisions is negligible compared with a foam cell size. The calculated mean free path for air calculated above is about 70 nm. Compared to the typical foam cell size (on the scale of a millimeter), it is safe to assume that the temperature of the insulation gas and the neighboring foam wall are the same. The Knudsen number (Eq. 8.10) is a dimensionless number that characterizes the pressure dependence of the thermal conductivity of a gas where L is the length over which energy and momentum are transported—in this case the foam cell size.

$$K = \frac{I_o}{L} \quad (8.10)$$

The typical case as outlined above is the case where the Knudsen number is very small. However, in the case of very low pressure or very small L (cell size) the pressure and corresponding temperature of a cell gas at any point will be more nearly the same since direct (or specular) and diffuse reflection of gas molecules off of the cell wall surface will be effectively isotropic (or more so) and no surface will be significantly hotter than any other. Thus, at very small foam cell size, less than 100 nm, the foam is effectively acting as if the gas has a lower ratio of heat transport to temperature gradient than would be expected. In the limit of this phenomenon, the insulation foam with a very large Knudsen number would appear to be a foam with evacuated cells and the K_{gas} of Equation 8.7 would tend toward zero.

As will be discussed Section 8.5, this phenomenon has been a research path numerous academic and industrial laboratories have pursued to most influence insulation technology. Some exotic technologies such as aerogels and xerogels [68–70] have provided very small pore sizes, but generally have relatively poor structural integrity and high cost. Obtaining very small pore sizes in conventional insulation materials such as polyurethanes have proven difficult without sacrificing low foam density that then causes an undesirable increase in the K -factor contribution from solid conduction.

8.5 TRENDS IN RIGID FOAMS TECHNOLOGY

While the patent literature is notably poor at providing insight of fundamental science, it is the clearest way of understanding the future of a technology and market [71, 72]. This is because the patent literature represents a sizable investment by a company or individual on what is believed will be desirable by customers and market

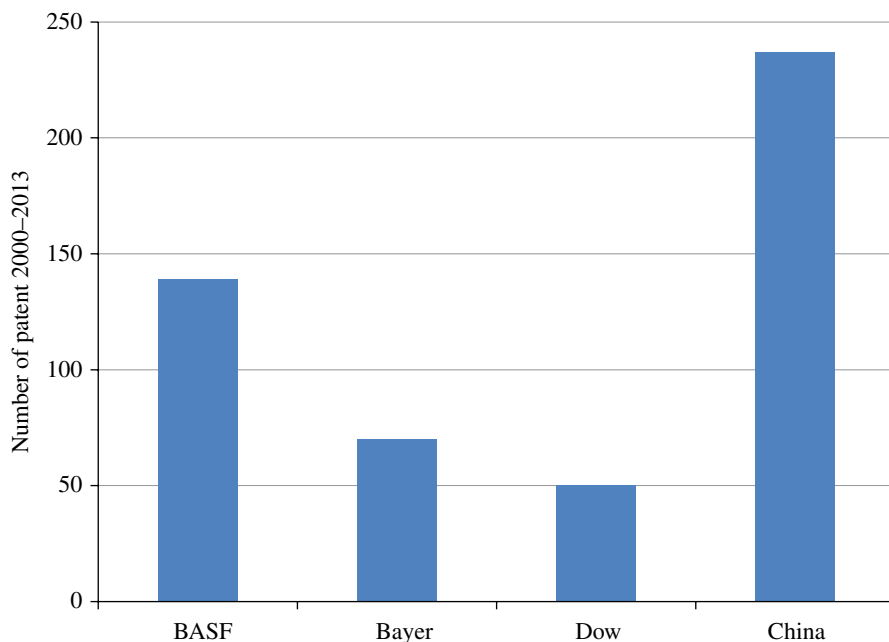


FIGURE 8.23 Relative patent activity on polyurethane insulation foams by three large polyurethane chemical producers and patent activity written in Chinese.

competitors in the next generation product. Further, defense of a patent asset requires that the technology on which a patent is based must be protected by patent prior to its commercial introduction.

While a single patent may not be instructive as to the direction of future innovation, a clear trend in industrial patent activity can be unmistakable. Figure 8.23 shows the patent activity of several large multinational polyurethane feedstock providers over the years 2000–2013 on the subject of insulation foams from polyurethanes. In this analysis, the patents filed in the Chinese language represent the activity within the sizeable Chinese market by Chinese companies. For perspective, the total number of issued patents found within the search parameters was 1451; therefore, it is clear that there are a large number of patents not accounted for by this analysis. Despite this, it is likely that the preponderance of unaccounted for patents will reflect the activity of these highly experienced and influential participants (i.e., Dow, BASF, and Bayer) within the polyurethanes market. While all of the illustrative market participants are actively patenting technologies to protect current and future market strategies and commercial opportunities, BASF is clearly the technology leader and believes that their technology insures future market strength. Also notable about Figure 8.23 is that companies patenting in the Chinese language are more concentrated in rigid foam technologies than in the same analysis for flexible foams discussed in Chapter 7.

Figure 8.24 shows that the majority of issued patents are concentrated around improving properties that define rigid foam applications and those that are required

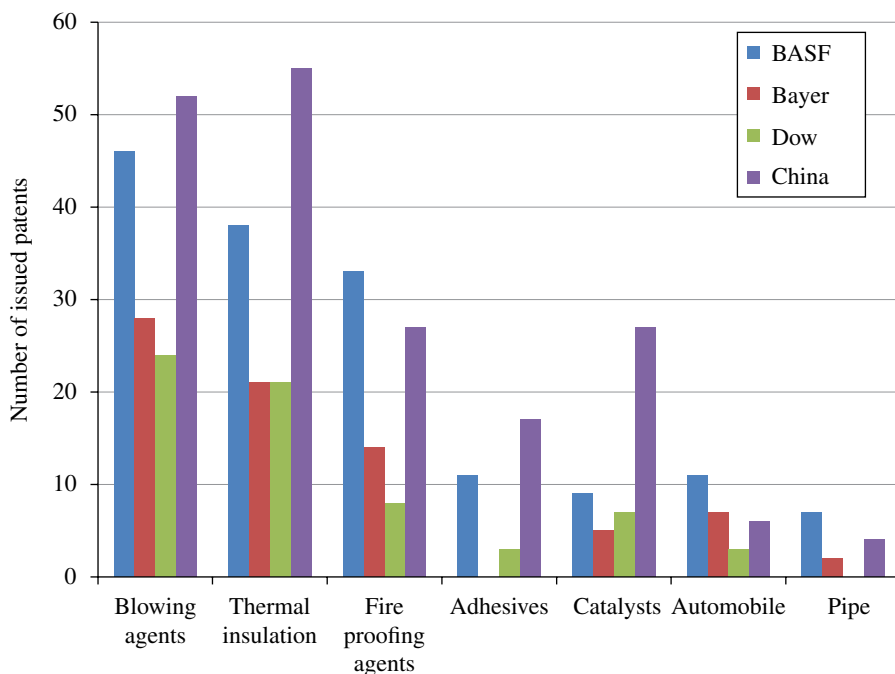


FIGURE 8.24 Patent activity of three large polyurethane chemical producers in the field of rigid foams by topic. (See insert for color representation of the figure.)

by regulation. Dow, BASF, Bayer, and Chinese-based companies all have shown a strong desire to invest in protecting future technologies associated with blowing agents and improved insulation properties. In this analysis, it is likely that there is some overlap between categories, since blowing agent technology can strongly impact thermal insulation properties as discussed in Section 8.3. In addition, it is apparent that fire proofing of polyurethane foams is a patent field of strategic importance to all commercial concerns related to rigid insulation foams for construction applications. Among smaller but significant concentrations of rigid foam patenting are technologies associated with advantaged catalysts and automotive applications. This activity and its intensity are common to that found in flexible foams. While flexible foams for automotive applications are primarily associated with seating, headliners, instrument panels, and carpet underlayment, rigid foam applications are usually poured or cut from buns for filling of body structural members for the purpose of structural reinforcement (Dow, Bayer), as a lightweighting component for a composite structure (BASF, Bayer, China) or as a lightweighting component of decorative or aerodynamic attachments like spoilers (Bayer, China).

Protected catalyst technology by Dow is generally around specific formulations for obtaining desirable cure schedules or physical properties, catalyst groupings for particularly effective processes using double metal cyanide alkoxylation catalysts, or catalyst packages for making isocyanurate foams. Chinese patents protect particular

catalysts for use in rigid foam recycle, low-toxicity catalysts, catalyst compositions promoting short demolding times for appliance operations, and efficient foaming catalysts with functionalized seed oil triglycerides for the purpose of making a rigid foam. BASF patenting on catalysts is primarily preferable compositions for the making of structural boards, shelf stable formulated systems, and systems tuned for improved adhesion to pipe surfaces. Bayer has activity patenting improved polyol production for rigid foam application, improved productivity making composite construction panels, shortened demold times for appliances, and double metal cyanide based catalysis for the production of polyether polyols for rigid foams.

Technology trends for future polyurethane rigid foams advancements appear to be highly incremental and existing line extension improvements. It is useful to understand this fact, and equally important to understand what is not being worked upon. Gaps in activity can represent opportunities that are being missed by “the herd” or traps to those uninitiated on the difficulty and risks of bringing forward new technologies for a very conservative market place. The current analysis does not predict what the future will hold, but it is telling that taking advantage of the Knudsen effect for improved gas thermal conductivity for foam *K*-factor does not appear in this analysis of polyurethane technologies. Similarly, although there has been significant industrial and academic activity in the area of seed oil feedstocks for polyurethane synthesis, it barely registers as a field of pursuit in the patent literature of rigid polyurethane foams. It would appear that the primary driving forces for future rigid foam technology differentiation are in order (i) energy improvement, (ii) productivity increase, (iii) cost reduction, and (iv) recycling.

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POLYURETHANE ELASTOMERS: MANUFACTURE, APPLICATIONS, MARKETS, AND TRENDS

Of the nearly 400 billion pounds of plastic produced every year, about 6% of that total is polyurethane (PU) and about 15% of that 6% is used purely for elastomer applications (Fig. 9.1). PU elastomers are very high performing within the general class of synthetic materials, and their applications run the gamut from footwear, to automotive body panels, truck bed liners, roller blade wheels, polishing pads for integrated circuit production, gaskets, blood bags, cattle ear tags, and polymer films. They are particularly specified when abrasion resistance, tensile strength, dynamic properties (periodic stress/strain), and low-temperature properties are paramount. They are usually not selected for applications where price is overriding, where routine temperature service greater than 120 °C is required, or where resistance to particular solvents is expected.

The PU elastomer business is divided into thermosetting elastomers that are cross-linked and made by casting techniques, thermoplastic that are made by reactive extrusion techniques, and elastomeric fibers that are made via numerous methods but generally spun from concentrated solutions. The fiber markets are handled separately since the applications are quite divergent from the other elastomers produced. Of thermosetting and thermoplastic PU (TPU) elastomers, the approximate ratio for their production and consumption is about 3:1 (Fig. 9.2) [1]. Apart from fibers, the large producers of PU building blocks are significant participants in the PU elastomer business, most of them having a global presence in this market. However, there are numerous (thousands) of much smaller participants in the PU market that have niche product or regional presence and can compete quite effectively within specific

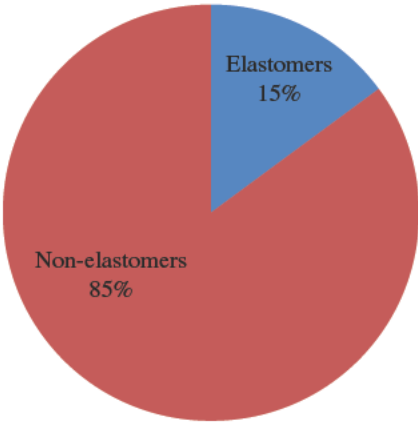


FIGURE 9.1 Approximate volume relationships between polyurethane elastomers and all polyurethanes consumed.

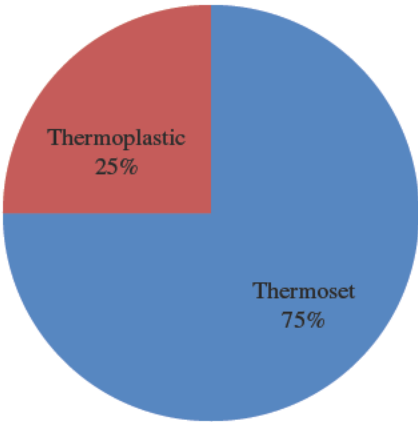


FIGURE 9.2 Approximate volume relationships between polyurethane thermosetting elastomers and thermoplastic polyurethanes consumed.

segments. Further, what concentration does exist within the PU elastomer business may in the future be prone to dilution since commoditization of products makes them less attractive to large publically held manufacturers.

9.1 REGIONAL MARKET DYNAMICS

The PU elastomer business, like the other PU businesses, is in flux due to the growth of the Asian manufacturing economies, and the movement of production assets to Asia (Fig. 9.3) [2]. At the same time, the growth of production capacity globally and regionally is not clearly in balance now, and may be more or less so in the future.

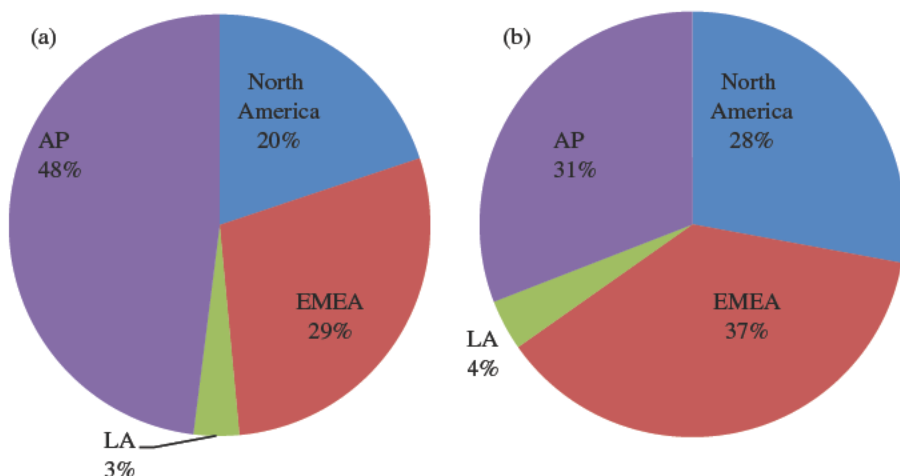


FIGURE 9.3 Approximate geographical industrial consumption of polyurethane elastomers for years (a) 2012 and (b) 2005. The graphs reflect migration of manufacturing to low-cost environments. The distributions do not reflect end-use consumption. AP, Asia-Pacific; EMEA, Europe, Mi-East and Africa; LA, Latin America.

This is most clearly illustrated by the PU elastomer fiber market that has seen prices go from \$10–12 per pound of fiber to \$4–5 per pound of fiber in a span of about 10 years. This deflation is occurring despite the inherent costliness of PU fiber processes and a global growth rate of about 6% per annum. PU elastomeric fibers will be covered in detail later in this chapter, but the remarkable commoditization of chemicals and products is also apparent in the case of PU elastomers.

The regional dynamics of PU elastomer markets are strongly influenced by macro-economic factors of overall economic activity that in turn influences the more direct factors of asset utilization within the PU industry [3]. This is usually measured by comparing the ratio of production capacity and product consumption as a function of history, and projecting with more-or-less confidence into the future based on announced plant shutdowns, expansions, and new capacity. The data in Figure 9.4 show the trend and projection in both Europe and Asia for oversupply of isocyanates. While this analysis does not cover polyols, isocyanates are of course required for every PU elastomer, and the variety of polyols for elastomers is significantly more varied, complicating what should be a simple point. That is, as long as there is oversupply in the PU industry, prices will be depressed for feedstocks as well as final products [4, 5]. Should the global economy pick up substantially, a condition of short supply of feedstock could emerge, as was observed in the early years of the analysis of Figure 9.4, and prices could rise as will company profitability. However if there is capital for expansion, manufacturers may gamble by adding still more capacity in an attempt to corner more revenues in a potential boom, and frighten off capital-poor competitors from gaining economic health by raising prices [6, 7]. Thus, the relatively dramatic point-to-point fluctuations of Figure 9.4 reflect the convolutions of many factors, both intentional and unintentional, within the industry.

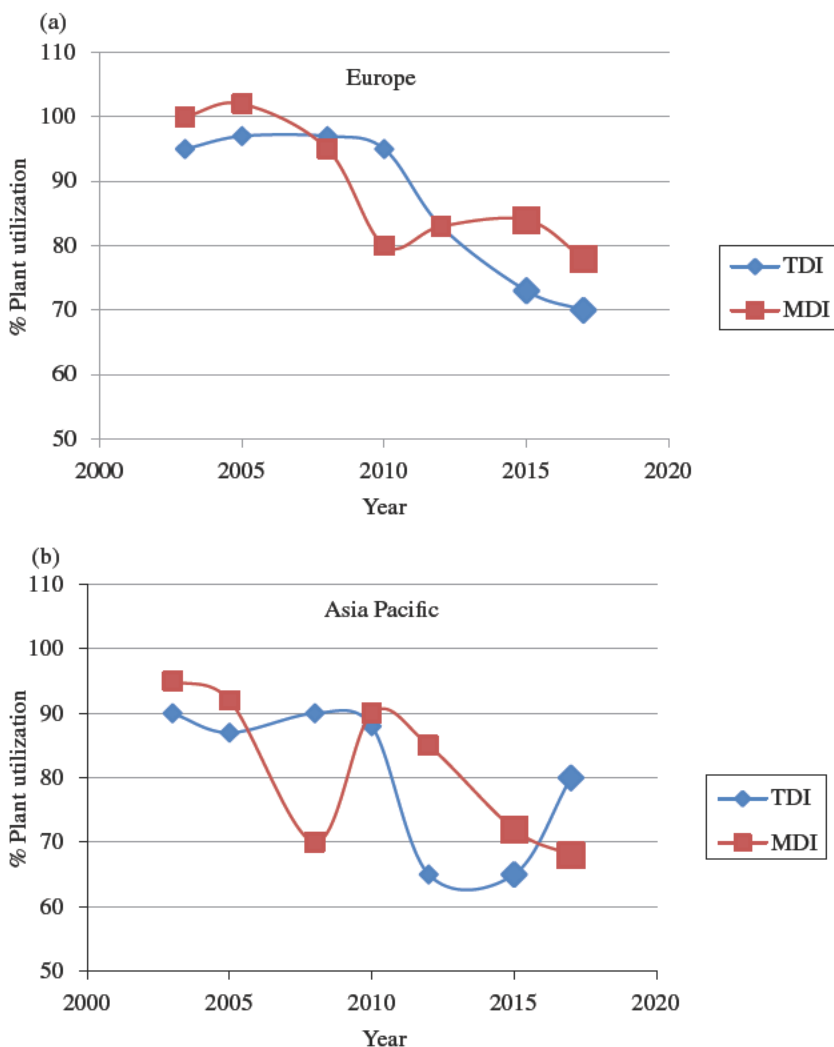


FIGURE 9.4 Capacity utilization for isocyanate production in (a) Europe and (b) Asia-Pacific. Low asset utilization results in low prices or production assets being shuttered. Larger symbols are projections.

As alluded to earlier, while the number of applications that PU elastomers can be applied to is quite large, the elastomers themselves can be conveniently divided into being thermosetting or thermoplastic. The ratio of their consumption is about 75% thermoset and 25% thermoplastic. While it is impractical to break regional consumption into relatively small application segments, it is still informative to simplify the categories into just thermosetting and thermoplastic elastomers. Figure 9.5 shows the changes in regional PU elastomer consumption as certain key segments, particularly footwear, have transferred manufacturing from Europe to Asia. The mature economies

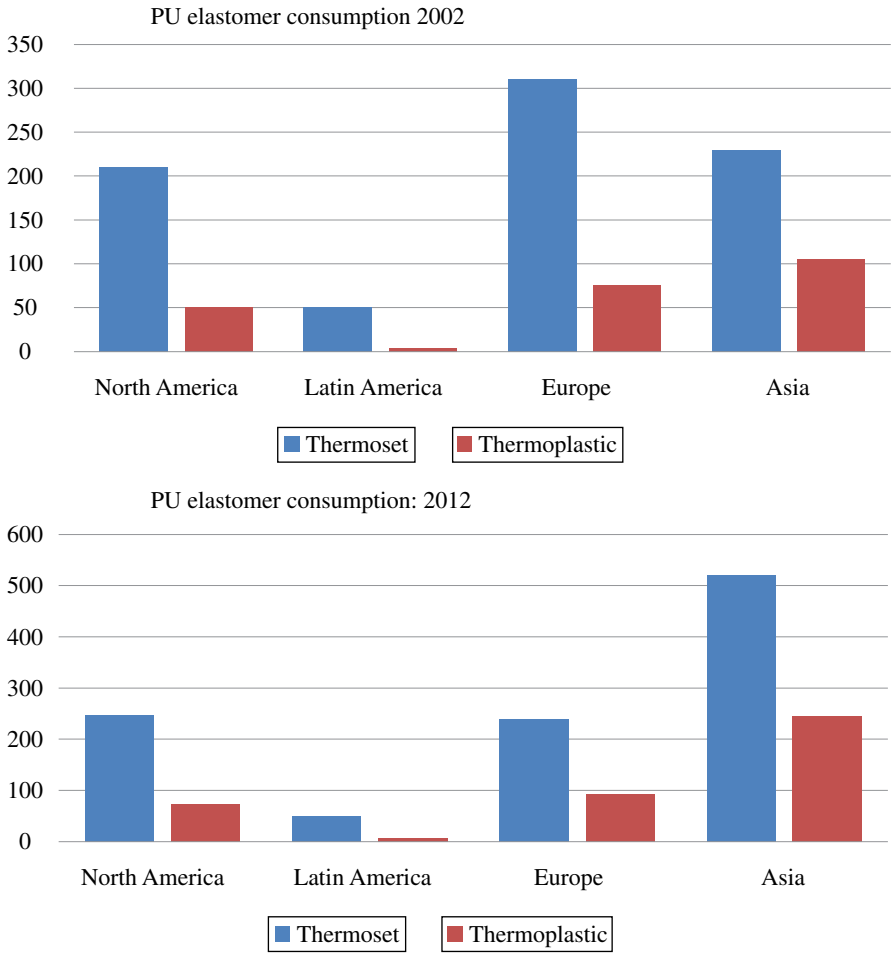


FIGURE 9.5 Regional industrial consumption of PU elastomers for the years 2002 and 2012 reflecting the migration of thermosetting elastomers, especially for shoe soles, to Asia. Units are MM lbs. (*See insert for color representation of the figure.*)

of Europe and North America (dominated by Western Europe and the United States, respectively) have nearly identical proportional consumption of thermosetting to thermoplastic elastomers. That consumption is somewhat skewed toward thermoplastics due to disproportionate use of thermoplastics within the automotive industry [8].

9.2 APPLICATIONS

Elastomer applications are varied, and it is difficult to draw sweeping generalizations. It is especially difficult to provide meaningful geographical data regarding consumption since the applications are globally relevant to consumers, but manufacturing of

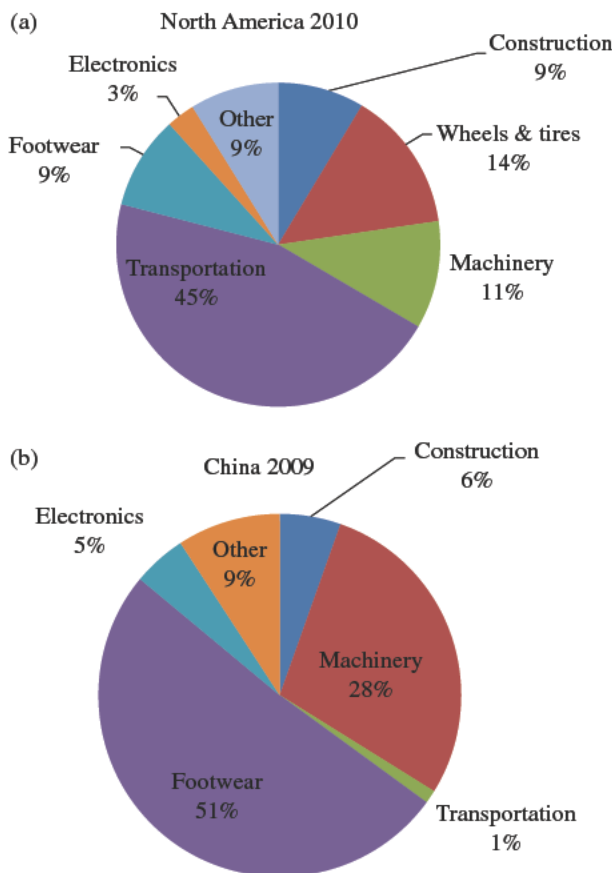


FIGURE 9.6 Volume fraction industrial usage of polyurethane elastomer in (a) North America in 2010 and (b) China in 2009.

specific products, such as footwear, is highly concentrated (in China). Another development has been the near disappearance of reactive injection molding (RIM) applications from the automotive segments, and its stagnant market development in nonautomotive applications.

Segmentation of applications by regional production exemplifies the changing global concentration of low-cost manufacturing of smaller devices and parts in low-cost economies, versus the high-cost manufacturing but dominant commercial markets in developed economies (Fig. 9.6). The dominance of transportation-related applications in North America reflects the compatibility of higher cost materials with more complex value-added assembly manufacturing. By contrast, the dominance of PU elastomers for footwear in China demonstrates the importance of low-cost manufacturing and the reduced impact of transportation of small items to final consumer cost. This macrotrend is further illustrated by the decline of PU footwear manufacturing in Western Europe as the opposite trend emerged in China (Fig. 9.7).

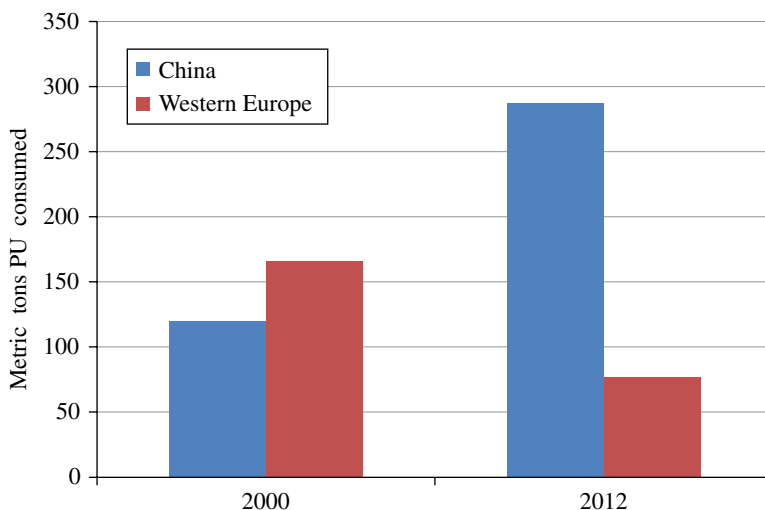


FIGURE 9.7 Consumption of microcellular polyurethane elastomer primarily used in footwear applications comparing data for Western Europe and China for the years 2000 and 2012 [9]. (See insert for color representation of the figure.)

9.2.1 Footwear

The footwear segment is a large and varied market and probably worthy of a more thoroughgoing treatment than can be afforded in this book. PU materials find uses throughout the footwear industry from work boots to ski boots, to running shoes, to high heels. Each segment has many optimized formulations based on cost and performance requirements. The footwear industry has moved quickly to provide ever greater performance in terms of low-temperature properties, abrasion resistance, and appearance. Certainly, one of the areas of greatest innovation has been the pursuit of excellent properties at lower densities resulting in lighter weight. Last, there has been significant progress in making TPUs with the required low modulus to result in adequate traction on all surfaces.

Relative to all polymer materials, PUs accounts for only about 6% of the total shoe-soling materials used. This still accounts for over 1 billion pounds of PU in 2011, but by comparison is dwarfed by materials such as polyvinylchloride (~5 billion pounds), natural vulcanized rubber (about 4 billion pounds), the tri-block copolymer of styrene–butadiene–styrene (SBS) also referred to as thermoplastic rubber, TPR (about 2 billion pounds), and ethylene vinylacetate (“EVA”, about 1.5 billion pounds). For perspective, the same amount of PU is used as is for leather shoe soling. PU is favored by shoe designers for its excellent low-temperature flexibility, very good wear properties (low abrasion), and the ability to produce it at a wide variety of densities by introducing porosity.

The PU component is broken up into thermosetting PU produced by injection molding/microcellular methods, and those using TPU. The ratio for these is approximately 4:1 (Fig. 9.8).

Thermosetting PUs for footwear applications are usually made from preformulated urethane systems developed to make a specific product with a designed hardness,

Polyurethane consumption by footwear markets – 2011

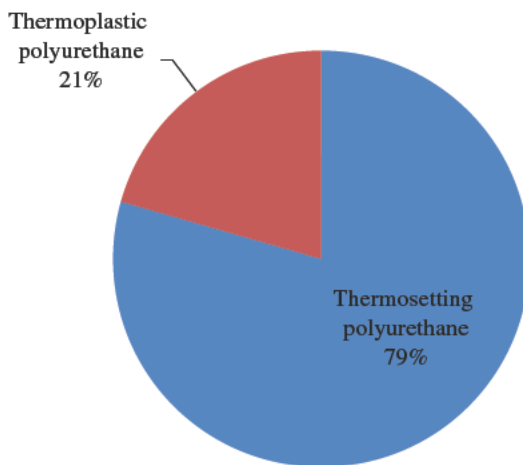


FIGURE 9.8 Approximate volume fraction consumption of thermoset versus thermoplastic polyurethane elastomers for footwear.

density, cost, and wear performance. Many shoe sole manufacturers begin with a system called a quasiprepolymer [10, 11]. A quasiprepolymer is essentially a prepolymer (see Chapter 2 and Section 9.2.2.1) with excess isocyanate. To make a quasiprepolymer, isocyanate (usually monomeric methylene diphenyl isocyanate or MDI or an added uretonimine modified MDI to maintain fluidity; see Chapter 3) is reacted with a 1000–6000 g/mol polyester or polyether polyol, or mixture of polyols with total NCO content range from 12 to 28% (see Chapter 2 for calculation of % NCO in a prepolymer). This makes one component of a two-component formulation. The other component will have a variable amount of polyol, chain extender, and additives such as blowing agent, stabilizers, dyes, and so on, to result in a final soling elastomer. Aliphatic polyester polyols certainly are the predominant choice for shoe sole systems. This is because of the higher toughness of polyester polyols in these systems, the attractive pricing of polyester polyols, and the ability to easily achieve the soft materials footwear applications demand for improved traction. The deficits of polyester systems relate to suboptimal low-temperature flexibility, the requirement to handle polyester polyols using heated lines to maintain adequate fluidity, and relatively poor polyester hydrolytic stability.

Some of the problems associated with shoe soles made using polyester-based PU formulations can be overcome using polyether formulations. In the past, polyether formulations were encumbered by an inability to fabricate soft elastomers that could meet durability requirements (see Table 9.1). Relatively long demolded times also hampered use of polyether systems from a manufacturing standpoint. Recent formulation and design advancements have solved some of these problems, and the attractive low-temperature performance, production handling, material feel, and price attributes of polyethers have led to significant growth. Although reliable data for the relative proportion of polyester versus polyether-based systems in shoe sole applications is

TABLE 9.1 Comparison of a polybutylene adipate ester and an ethylene oxide-capped polypropylene oxide polyether-derived shoe sole material

Property	Ester-based shoe sole	Ether-based shoe sole
Density (g/cc)	1.21	1.08
Shore A hardness	65	65
Tensile strength (N/mm ²)	28	11
Tear strength (N/mm)	83	59
Abrasion (mm ³)	80	350
Flex fatigue resistance (cycles at -0 °C)	>200 K	>200 K

lacking, it is unquestionable that polyester systems represent more than 80% of the PU shoe sole volumes, and it is also quite likely that polyether systems will continue to gain ground as systems with better performance are created. The use of polyether systems will also increase as designers try to obtain the best of both polyester and polyether worlds by mixing the systems. There is evidence [12] that polyester/polyether mixtures actually result in systems handicapped by the weaknesses of both systems rather than compensated by the strengths, but this will not stop attempts at innovation by artful blending of components.

PU footwear made from prepolymer or quasiprepolymer two-part formulations are pumped from their respective tanks and mixed by a high-speed (6,000–20,000 rpm) mixing mechanism. The mixed and reacting PU is then either injected or poured into a mold to form the desired shape. The mixing head may have numerous ports allowing for sequential injection of different formulations to get specific performance, or gas to introduce porosity and reduce density, or different dye packages to achieve specific cosmetics [13].

Until recently [14], footwear made from TPUs had been limited to injection molding of relatively hard footwear components such as ski-boots and base plates for soccer cleats (and the cleats as well), air bags for shoe cushioning, and decorative appliques for instance. This was because preparation of sufficiently soft TPU had been unobtainable in pellet form without the pellets melding upon sitting in a bag or a hopper. Minimum hardness conventionally obtained for TPUs had previously been about Shore A 70. Upon superficial inspection, a Shore A 70 TPU pellet will seem soft, but it is not soft or flexible enough for shoe sole application. To obtain adequate comfort and traction on a smooth surface, shoe soles typically require Shore A from 45 to 65. Breakthroughs in TPU formulation and production have in part eliminated these restrictions, and TPUs are becoming more freely employed for various footwear constructions. In some cases, this means use of conventional injection molding techniques. In other cases, to avoid degradation of the TPU due to overheating, manufacturers essentially pour the TPU melt into a standard casting mold rather than heating the plastic to a sufficiently high temperature that the viscosity is low enough to be injected.

Formulation and innovation of PU for footwear application must always be performed with respect to specified tests. Specified tests provide a common framework for comparison of different materials and also precisely prescribe the methods for measurement. In the footwear industry, certain tests and measurements are fundamental

for understanding suitability. Such tests include density, hardness (Shore A for moderately soft to moderately hard, or Asker C for very soft), abrasion resistance, tear resistance, and compression force deflection. Other tests may be required by specific manufacturers or for specific applications, or more prevalent in one region than the other. Other tests such as “feel” are subjective and resistant to quantification. Table 9.2 lists down some of the commonly employed tests.

TABLE 9.2 Representative standard tests for characterizing, comparing, and ranking materials, including polyurethanes for footwear application

Test	Standard description
ASTM D 3851-07	Standard specification for urethane microcellular shoe soling materials; provides a list of standard tests for specific areas of performance and a table of typical values for three hypothetical grades distinguished by tensile strength and abrasion resistance
ASTM D624	Test method for tear strength for vulcanized rubber and thermoplastic elastomers
ASTM D1938	Test method for tear propagation resistance by trouser tear method
ASTM D 792	Test method for measuring density and specific gravity by displacement. Can substitute ISO 845
ASTM D1052	Ross flexural test—machine and sample preparation are specified. The test specifies test temperature of 23 °C; however, most manufacturers test at –10 to –20 °C for 100–300 K flex cycles to determine low-temperature flexural performance. Can substitute DIN 53543.
ASTM D2240	Test method for measuring durometer hardness. Can substitute DIN 53505
ASTM D5963	Standard method for abrasion resistance using a rotary drum abrasion covering the German DIN 53516 abrasion test.
ASTM D1630	Test method for abrasion measured by a footwear abrader—test uses a rotary abrader like Standard D 5963, but the specifics of the abrasion pattern differ.
ASTM D 395	Test methods for determining compression set
ASTM D575	Test method for measuring elastomer properties under compression. Can substitute DIN 53543.
ASTM D3137	Test method for measuring rubber hydrolytic stability. Simply a high humidity test measured at 85 °C after 96 h using <i>distilled</i> water. Results at nonneutral pH could be substantially different.
ASTM F2333	Standard test method for traction characteristics of the athletic shoe—sports surface interface—application specific test but does not require specific instrument
ASTM F2913	Standard test method for measuring the coefficient of friction for evaluation of slip performance of footwear and test surfaces/flooring using a whole shoe tester. Test requires precise control using specified piece of equipment and procedures.
ASTM F2370	Standard test method for measuring the evaporative resistance of clothing using a sweating manikin. Can be used to quantify breathability.
ASTM F1291	Standard test method for measuring the thermal insulation of clothing using a heated manikin. Can be used to quantify the insulative qualities of footwear.

TABLE 9.3 Design guidelines for the effect of a change in material property on wet and dry coefficient of friction

Polymer property		Effect on dry COF	Effect on wet COF
Modulus	↑	↓	↑
T_g	↑	↓	↓
Hysteresis	↑	↑	↓
Resilience	↑	↑	↑

For passing shoe manufacturer tests, formulation of shoe sole systems can be as much art as science [15]. Shoe soles have become highly complex structures in the case of athletic shoes, and very high-performance materials in the case of work and safety shoes. It would be futile to offer a shoe sole formulation or table of performance attributes that could be understood as anything other than illustrative. However, there is little doubt that certain properties are exemplary of many shoe soles, and that certain formulations possess components common to the application. From a fundamental standpoint, one can begin by drawing common relationships between material properties and critical shoe sole requirements [16–19]. For instance, a shoe sole must possess a preferred coefficient of friction (COF) on dry and wet surfaces. While a high COF may be preferable, maximizing the COF for the material may entail an unacceptable tradeoff in other dimensions. Table 9.3 offers the effect of designing material properties on this particular variable. While not all aspects of this comparison are intuitively consistent (i.e., varying effects of resilience and hysteresis that are normally coupled), they are generally found to be true by experience. This suggests that the polymer structural characteristics, which are normally reflected in consistent polymer properties, are not being *tested* consistently and therefore provide relationships that are apparently at odds with each other [20].

An example of a PU shoe sole formulation based on polyester polyols and associated properties is given in Table 9.4. The effects of ester hydrolysis are pronounced on tests that stress the degree of network continuity that hydrolytic chain scission most effects. An example of a PU shoe sole formulation based on polyether polyols and associated properties is given in Table 9.5.

TPU for shoe soles only represents about 20% of the total PU shoe sole market, but the total PU market is only about half as large as the feedstock nonvulcanized SBS copolymer. This makes TPU only about one-seventh as large as the competitive TPR SBS (Fig. 9.9) [21–24]. While being a small fraction of the shoe sole market, it still represents about 380 million pounds of PU consumed—a fairly significant absolute volume of material. The general details of PU manufacture will be covered later in this chapter. TPU is commonly considered a high-performance material of shoe construction due to its low-temperature flexibility, good abrasion and scratch resistance, and its ability to fill even very complex shoe molds with very high fidelity resulting in desirable aesthetic values. These attributes have made TPUs

TABLE 9.4 Example shoes sole formulation based on a polyester quasiprepolymer and associated properties

Component	Weight	Comments
Quasi prepolymer side		
MDI monomer	54.6	18% NCO 125 g/iso equiv
Uretonimine modified MDI	6.7	169 g/iso equiv
Polyester polyol of ethylene glycol/diethylene glycol and adipic acid	32.4	1000 g/OH equiv
Polyester polyol of diethylene glycol/trimethylolpropane and adipic acid	2.7	935 g/OH equiv lightly branched
Polyether polyol triblock of PO/EO end caps 20% EO by weight	3.4	2000 g/equiv diol
Benzoyl chloride	0.2	Acid stabilizer
Polyol/chain extender side		
Ethylene glycol	7.67	Chain extender to define the hard segment 18 g/equiv OH
Polyester polyol of ethylene glycol/diethylene glycol and adipic acid	90.4	1000 g/OH equiv
Water	0.35	
33% Triethylene diamine in ethylene glycol	1.43	Catalyst
Silicone surfactant for shoe sole application	0.13	Helps stabilize density decreasing bubbles created by isocyanate water reaction.
Properties		
Cream time (s)	8	
Gel time (s)	21	
Minimum demold time	3' 15"	
Density (molded, g/l)	550	
Hardness (shore A)	55	
Tear strength (N/mm)	7.2	
Tear strength after hydrolysis test ISO 20345 (N/mm)	6.4	
Flex test (DIN 53543) (cycles)	100,000	
Flex Test after hydrolysis test (ISO 20345)	30,000	
Abrasion (mm ³)	80	

Shoe sole formulation based on polyester polyols.

Quasiprepolymer/polyol ratio = 94/100.

desirable components in the construction of high-quality work, safety, and hiking shoes [25–27]. Limiting factors have been cost, and by relatively poor slip performance associated with difficulty making TPU at low enough hardness while still meeting customer requirements. To lower cost and reduce polymer hardness, plasticizers have been added.

Most TPU shoe soles are based on polybutylene adipate polyols with monomeric MDI and butanediol chain extender [28, 29]. These materials have very good properties, good clarity allowing for easy dyeability, and relatively low cost.

TABLE 9.5 Example polyether polyol shoe sole formulation based on a polyether soft segment

Component	Weight	Comments
Quasi prepolymer side		
MDI monomer	65	18.4% NCO 125 g/iso equiv
20/80 EO//PO triblock polyether polyol OH # = 27.5	15.5	Diol 2040 g/equiv OH
14.7/85.3 EO//PO triblock polyether polyol OH # = 27.5	15.5	Glycerine-initiated 2040 g/equiv OH
Dipropylene glycol	4.0	67 g/equiv OH
Benzoyl chloride	0.01	Acid stabilizer
Polyol/chain extender side		
20/80 EO//PO triblock polyether polyol OH # = 27.5	63	Diol 2040 g/equiv OH
14.7/85.3 EO//PO triblock polyether polyol OH # = 27.5	15	Glycerine-initiated 2040 g/equiv OH
17.6/83.4 EO//PO triblock polyether polyol OH # = 21.3 40% SAN grafted SAN copolymer	10	
1,4 Butane diol	8.75	Chain extender
33% triethylene diamine in ethylene glycol	1.5	Catalyst
Silicone surfactant for shoe soles	0.15	
Polybutadiene liquid	1	Abrasion reducer
Water	0.43	
Dibutyltin dilaurate	0.02	Catalyst (for formulations able to use tin catalyst)
Properties		
Cream time (s)	8	
Gel time (s)	16	
Minimum demold time	3'30"	
Density (molded, g/l)	550	
Hardness (Shore A)	51	
Tear strength (N/mm)	5.2	
Flex test (DIN 53543) (cycles)	>100,000	
Abrasion (mm ³)	130	

Quasiprepolymer/polyol ratio = 67/100.

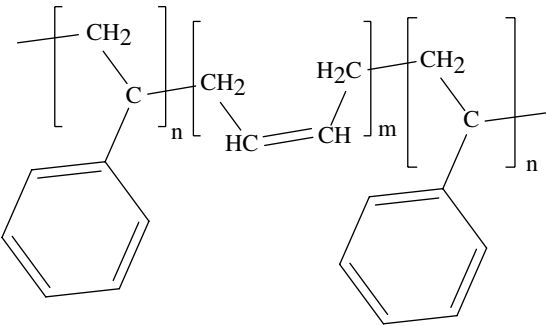


FIGURE 9.9 Styrene–butadiene–styrene triblock copolymer, the major component of TPR used in shoe soles.

TPR, which is compounded SBS copolymer (Fig. 9.9), is the dominant TPR within the shoe sole market. Compounding components vary, but sulfur and zinc oxide are common additives used to produce some crosslinking among the SBS chains through the butadiene moieties. Along with shoe soles, TPR finds common usage in tire construction. Several positive attributes of TPR include (i) price, (ii) durability, (iii) good aesthetic, and (iv) relatively easy processability [30]. This last point is a very clear advantage in the eyes of manufacturers since much less can be asked or expected of machine operators filling molds, especially in operations in emerging economies [31]. This is particularly evident when it is considered that along with beneficial properties, TPRs suffer inferior tensile properties, abrasion resistance, resilience, slip resistance at equivalent hardness in comparison with TPUs.

9.2.1.1 Trends in Footwear Applications Although consumers rarely ask questions about their shoe sole materials, it would surprise many if informed about the level of innovation and technology that is invested into shoe soles. While patenting on shoe sole technology is a global pursuit, since 2000 the majority of patents have been filed from concerns located at the shoe manufacturing centers. Since the year 2000, of the 525 patents filed specifically on PU shoe soles, 145 were on behalf of companies entirely of Chinese origin. Among large global manufacturers, BASF filed 48 patents on shoe sole technology, Bayer 29, and Dow Chemical 12. The technology covered in these patents relates to improved hydrolysis, improved abrasion, improved cosmetics and design, improved manufacturing, electrically conductive shoe soles, shoe soles of complex density gradients, shoe soles with very low density, improved mold release agents, and odor mitigation. Certainly, the predominant technology trend is pursuit of high performance at reduced densities [32, 33]. The evidence of this trend is validated by casual inspection of shoes displayed at retail outlets.

9.2.2 Nonfootwear Elastomer Applications and Methods of Manufacture

Apart from shoe soles, elastomer categorization relative to applications is an exercise in rapidly diminishing returns. Analysis of large sectors such as “transportation” reveals that the applications are myriad, none of which by themselves would merit significant exposition, or are much like other unrelated applications. A partial list of application and application areas is provided in Table 9.6. For instance, the requirements of conveyor belts [34, 35] and tire treads [36] are quite similar but apply to vastly different consumers, and compete with different companies and alternative materials. Rather, these applications are differentiated by their use of specific PU components and the way these components are then used to make parts. A graphical way of depicting these components of construction is shown in Figure 9.10.

9.2.2.1 Cast Elastomers From Table 9.6, it is clear that breaking PU elastomer technology down by applications (apart from shoe soles) is futile due to the sheer number of applications, the lack of property uniformity within each application, and the lack of volume domination within applications [37]. The custom nature of the applications and resulting formulations makes for a complex commercial

TABLE 9.6 A representative listing of polyurethane elastomer applications

Tire fill	Instrument panel covers	Pipe line pigs
Print rollers	Shock absorbers	Pipe line insulation
Conveyor belts	Non-pneumatic tires	Roof membranes
Roller skate wheels	Run-flat tires	Rubber tougheners
Cattle tags	Pump impellers	Mechanical polishing pads
Tooth brushes	Track and field surfaces	Suspension bushings
Blood bags	Potting/encapsulation	Railway pads
Medical devices	Water skis	Bicycle helmets
Seals	Bicycle seats	Electrical jacketing/tubing
Gaskets	Tool hand covers	Breathable films for apparel
Spray coatings	Belts and pulleys	Airline emergency slides

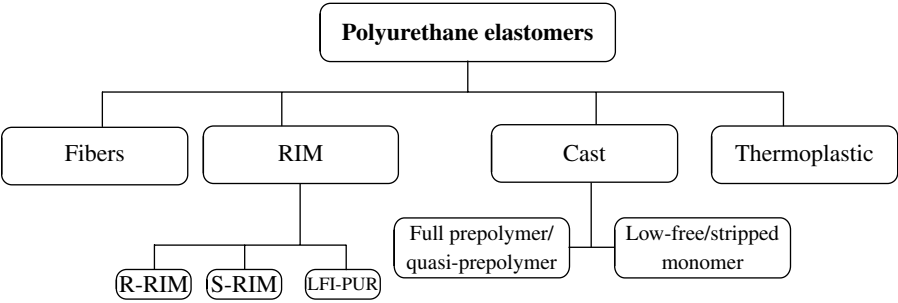


FIGURE 9.10 Segmentation of polyurethane elastomers not including footwear. Elastomers applied as coatings are also not included here.

environment. Since the applications are relatively small and dispersed among numerous end users, cast elastomers seems like an ideal commercial space for systems houses to flourish. Indeed, PU formulated system houses do occupy an important distribution channel. However, the availability of raw materials such as polyols, isocyanates, and curatives at low costs invites one-stop-shop distributors to serve as alternative lower cost middlemen, as well as for molders to try and fill the space of these middlemen, and to purchase directly from the large chemical manufacturers (Fig. 9.11). The ability of molders to choose their mode of purchase creates a very competitive market, and results in very rapid commoditization of formulation innovation or methods of production.

The choice of commercial relationship will also depend on the technical sophistication of individual molders and their interest in workplace health and safety controls. For cast PU elastomers, the primary means of production that has created equilibrium relationships among all of the participants have been via the use of prepolymer and stripped (or low-free isocyanate) prepolymer formulations.

For clarity, the prepolymer approach can be contrasted to the so-called one-shot approach. When using a one-shot approach, an elastomer producer will take a predetermined amount of polyisocyanates, polyols, curative (or chain extender),

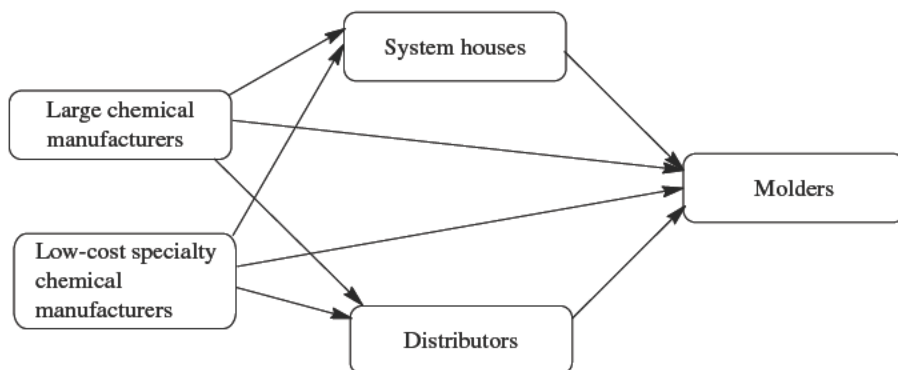


FIGURE 9.11 A simplified representation of polyurethane elastomer market positions.

and additives, mix thoroughly, and pour them into a mold where reaction proceeds to completion.

In a prepolymer process, polyol is reacted with a stoichiometric excess of isocyanate such that there is a minimal amount of polymerization that can occur since all the available hydroxyl groups are reacted with isocyanates, and there is no available hydroxyl functionality to react with isocyanate (Fig. 9.12) [38–40]. Temperature is controlled to minimize the extent of isocyanate–isocyanate reaction. These fully reacted polyols possessing isocyanate end groups then make up one side of a two-component formulation. The other side will usually constitute curative (chain extender) or polyol and chain extender and other additives.

From this process, four different prepolymer varieties have established themselves: the full prepolymer, the quasiprepolymer, the low free isocyanate prepolymer, and the stripped prepolymer [41]. These prepolymer varieties differ from one another merely in the amount of free isocyanate left in the prepolymer side to then be reacted with curatives or curatives and polyols (see Table 9.7).

In a quasiprepolymer preparation, a relatively small amount of polyol is added to a large stoichiometric excess of polyisocyanate as described in Figure 9.13.

While Figure 9.13 depicts the preparation of a TDI quasiprepolymer, MDI quasiprepolymers are commonly found and predominant in manufacturing environments trying to limit worker chemical exposure to isocyanates. The full prepolymer is characterized by a much lower content of free isocyanate that somewhat simplifies handling, but also limits the number of different materials that can be prepared from a single full prepolymer. The quasiprepolymer allows the molder to vary end products simply by varying the ratio of curative and polyol in the second component. The same can be accomplished to a more limited degree with the full prepolymer; but due to the low free isocyanate available, the molder will usually only add curative as a second component to build hard segment volume. While the full prepolymer and quasiprepolymer approaches have dedicated users in all geographies, it is more common for European molders to request quasiprepolymer systems and North American formulators to request full prepolymer systems.

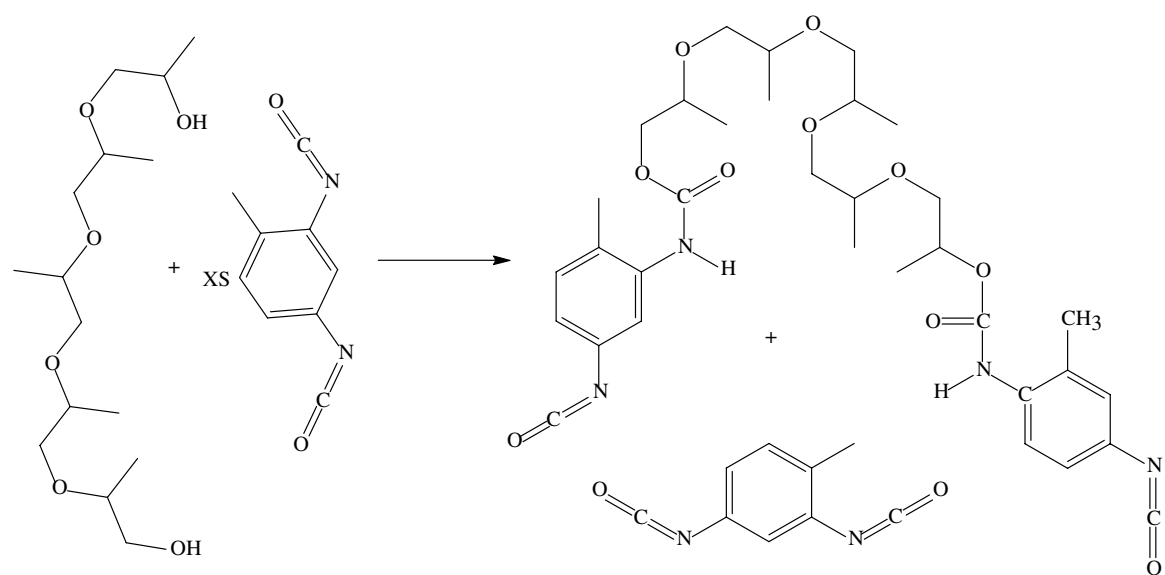
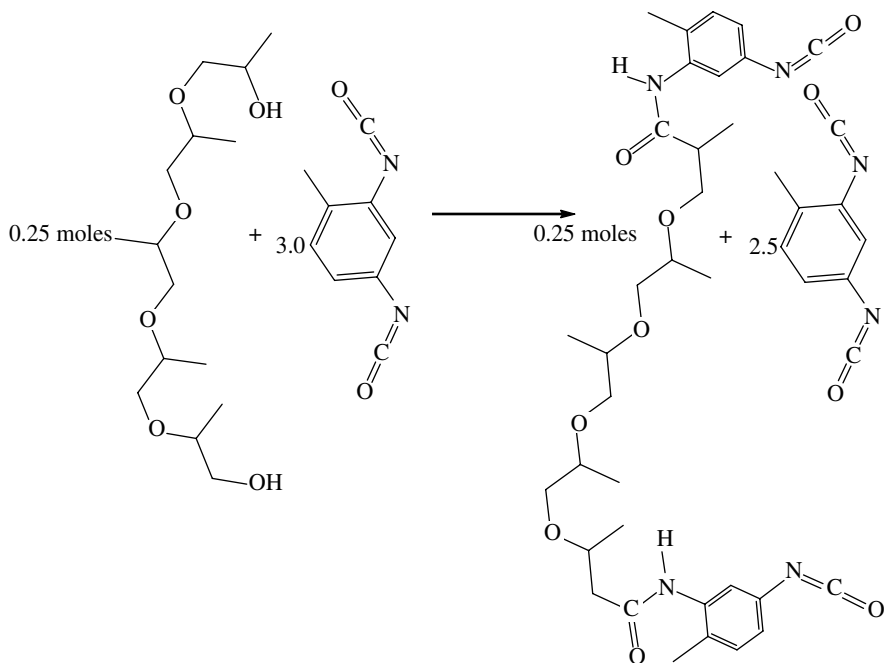


FIGURE 9.12 The prepolymer production concept.

TABLE 9.7 Characteristics of the types of commercially

Prepolymer variety	Amount of free isocyanate (%)	Comments
Quasiprepolymer	12–28	Requires formulating with polyol and curative—provides flexibility to molder to vary final elastomer properties
Full prepolymer	<12	Provides very high control to molder for a specific final polymer result, but each specific prepolymer can only make a single elastomer
Low free isocyanate	~1	Less expensive than stripped prepolymer
Stripped prepolymer	<0.1	Most expensive, lowest hazard, usually does not require isocyanate hazard labeling

**FIGURE 9.13** Example of the quasiprepolymer concept.

While full prepolymer and quasiprepolymer formulated systems are predominant in most cast elastomer applications, there is growing awareness, and in all geographies, that free isocyanate can present an undesirable exposure risk to workers in environments that might otherwise have acceptable environmental controls. For these customers, producers have created products having the excess isocyanate removed from the prepolymer. The thoroughness of the distillation will create either the low-free (monomer) prepolymer or the stripped prepolymer. There is not much reliable information on the relative volumes of low-free versus stripped prepolymer,

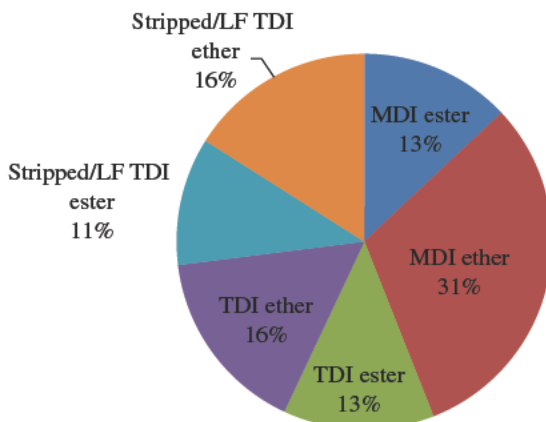


FIGURE 9.14 North American consumption of prepolymers by type.

and they are often considered as a single class. Further, due to the relatively greater difficulty distilling low vapor pressure MDI from prepolymer systems [42] the prevalence of stripped and low-free TDI prepolymers is much greater than the same for MDI. Figure 9.14 shows that the North American market for stripped/low-free prepolymers (all TDI based) is approximately 30% of the total prepolymer market.

The overall size of the prepolymer market is difficult to estimate with a high degree of confidence and available published market estimates are often unwarranted extrapolations from unrelated data. A reasonable estimate based on analysis of numerous sources is that the overall prepolymer market, irrespective of the isocyanate, is about 400 million pounds split about half between TDI and MDI with a trend toward increasing MDI incorporation. The choice of customers to use a low-free or a stripped isocyanate prepolymer is to some extent arbitrary, although two things are certain: (1) there is a substantial price increase, as much as \$1.0 per pound, in reducing free isocyanate from 1 to less than 0.1%, and (2) that stripped prepolymers do not have to possess warning labeling on their packaging, while labeling of low-free prepolymers varies from country to country [43–45]. For customers who are insensitive to labeling issues, the price differential drives them toward low-free prepolymers, since the absolute difference in resulting elastomer properties between low-free versus and stripped prepolymers is generally anecdotal, and likely reflects subjective preference.

The decision to use a quasiprepolymer or a full prepolymer has consequences that the molder must consider before making a process commitment. The basic equipment is common for both quasiprepolymers and full prepolymers except for the possible use of a third tank when working from a quasiprepolymer to vary curative and polyol volumes independently (Fig. 9.15). Other differences are provided in Table 9.8.

In no way representative of all full or quasiprepolymer systems, Table 9.9 provides a simple comparison of formulation and resulting elastomer properties. A representative experimental procedure for making prepolymers and making the cast mold plaque for testing is provided in the caption of Table 9.9. The simplicity of the procedure is largely responsible for wide adoption of cast elastomer techniques;

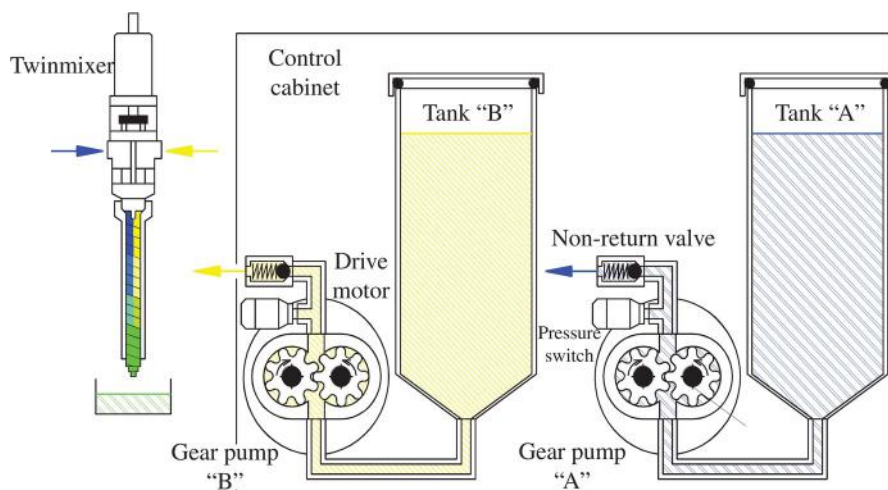


FIGURE 9.15 Simplified diagram of a cast elastomer molding system with two tanks. A quasi prepolymer system might often employ a third tank to allow for easy variation of curative and polyol. Reprinted with permission from Ref. [46]. © John Wiley & Sons, Inc.

TABLE 9.8 Differences between quasiprepolymer and full prepolymer systems and resulting elastomers

Property	Full prepolymer	Quasi-prepolymer
Viscosity	Higher (often solids)	Lower
Shelf-life	Longer	Shorter due to dimerization of MDI monomer
Exotherm during reaction	Lower (many fewer reactions to achieve cure)	Higher and may promote unwanted side reactions
Shrinkage during cure	Lower	Higher (due to greater exotherm)
Flexibility in making materials	Very low—one full prepolymer can make a very limited range of materials, usually just variation by changing curative	Very high by simultaneous variation of polyol and curative/chain extender/shorter turnaround times with equipment
Catalyst required	Often not when using aromatic amine curatives	Yes—requires high gelation activity
Mechanical properties	Usually better defined and more predictable	Also good but phase separation dynamics may be highly sensitive to process details
Low-temperature handling	Usually requires significant amount of heating of tank and heating of transfer lines	Much lower heating requirements
Worker exposure issues	Higher with TDI-based prepolymers, but otherwise lower due to lower overall isocyanate	Lower with MDI quasiprepolymer systems
Abrasion (at equal hardness)	Higher	Lower (due to resistance of hard segment)
Chemical stability [47]	Reported to be lower	Reported to be relatively better

TABLE 9.9 Cast elastomers formed at between 70 and 80 °C under N₂ for 3-6 h at desired NCO content

Component	Quasiprepolymer	Full prepolymer
Polyether polyol/	16% NCO (MDI)	12% NCO (TDI)
Curative/chain extender	BDO	MOCA
Hardness range (Shore A)	60–90	40 (Shore A)-60 (Shore D)
Tensile strength (Shore A) (psi)	4800	5400
Elongation at break (Shore A 90)	450	650
Compression set (%)	30	30
Ball rebound (%)	50	56

Extent of reaction determined by amine titration (di-*n*-butylamine) followed by degas at 70 °C. Prepolymers mixed with second part in a speed mixer followed by open-air cure at 100 °C in a heated mold followed by post-cure heating (annealing) at 100 °C in a convection oven.

TABLE 9.10 Applications defined by the typical shore a hardness required

Application	Shore A	Shore D
Papermaking rolls		70
Metal forming wiper dies		65
Mallet heads	95	55
Run-flat tires	95	
Solid tires	90	45
Metal forming die pads	85	40
Idler rolls	80	35
Abrasive handling pads	75	
Auto tire treads	65–80	
Silk screen wiper blades	60	
Door seals	55	
Inner tubes	50	
Printing rolls	25	
Rubber bands	20	

however, proper protection from exposure to isocyanates should always be employed. Elastomers made with process and formulation optimization can be employed in applications such as those listed in Table 9.10.

9.2.2.2 Thermoplastic Polyurethanes TPUs are widely regarded as providing the desirable properties of PU elastomers with the desirable processing of thermoplastics. This means that TPUs can be processed by extrusion, injection molding, casting, and casting from solution. TPUs achieve this processing flexibility by avoiding crosslinking of the polymer chains; other PU systems do not achieve this processing flexibility. By and large, all building blocks used for making TPUs have a functionality of 2.0. It has been shown that TPU processing is not noticeably harmed when employing soft segment functionalities as high as 2.05 (by incorporation of small amounts of a three-functional polyol), but soft segment functionalities as low

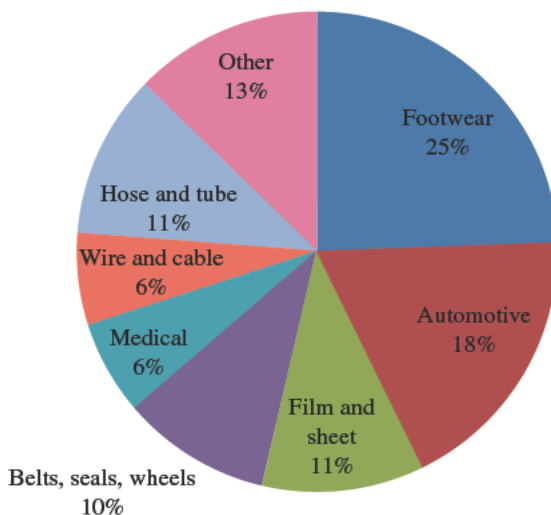


FIGURE 9.16 Global segmentation of the 2012 TPU market by consumption volume.

as 2.1 cannot be processed as a melt [48]. As discussed in the Section 9.2.2.1, the market for TPUs is also fractured among applications (Fig. 9.16) and customers. Each application segment has numerous subsegments demanding unique solutions. In keeping with China's dominance in parts manufacturing, and particularly in footwear, it is consistent that China should be the dominant consumer of TPUs, and the growth of its consumer culture coupled with increasing demand for automotive transportation assures that China should continue to see high TPU growth rate (estimated at about 8% per annum) for the near future.

While production of TPUs is not very technologically advanced, it is capital intensive requiring large twin-screw extruders for reactive processing, and a significant amount of specialized processing equipment for before and after the reactive extrusion [49]. Further, since the number of applications and requirements within each application segment are numerous, the requirement for rapid and frequent formulation change-over and inventory storage complicates manufacturing and customer service. North American production of TPU is dominated by Lubrizol Corporation manufacturing about 70% of North American production. The other producers are low-cost global producers of TPU feedstocks (particularly, MDI required for its 2.0 functionality) such as BASF, Bayer, and Hunstman. The same is true for Europe, although they are joined by COIM, a major polyol producer. These same producers also maintain a footprint in China, often with local partners. Yantai Wanhua, China's largest producer of MDI, is also the largest producer of TPU in China, but for perspective, in a more fractured market, this only reflects about 15% of all Chinese production (Fig. 9.17).

The capital requirements for TPU production are not conducive to service by formulation system houses operating on a low capital asset business model. However, production of TPU grades for large accounts can be made more profitable by selling additional inventory to smaller, more difficult-to-service accounts through distributor channels (Fig. 9.18). The success of this structure is complicated by the drive to

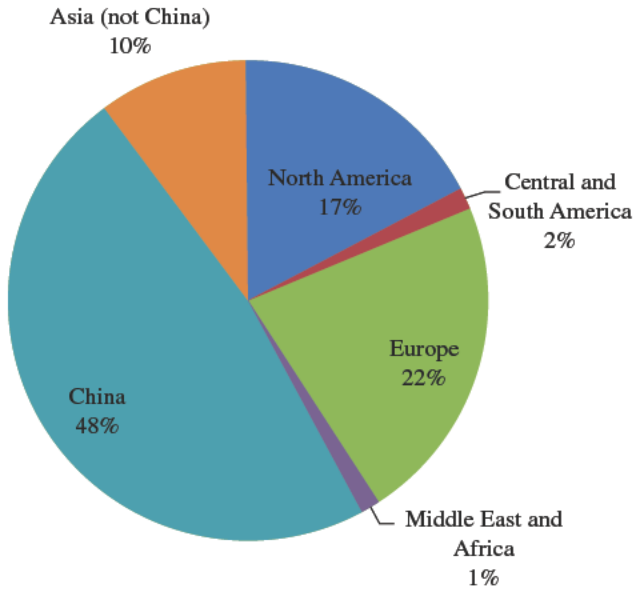


FIGURE 9.17 Segmentation of the 2012 global TPU market by region.

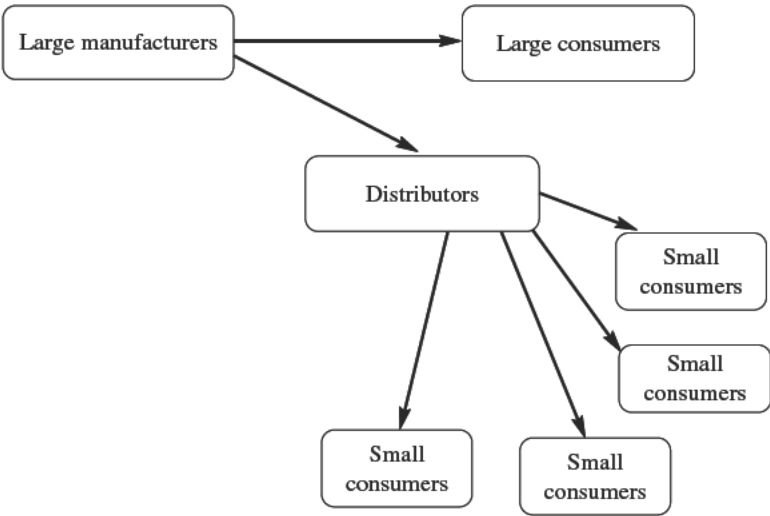


FIGURE 9.18 Simplified diagram of the commercial relationships between manufacturers and molders of TPUs. Systems houses do not participate in this segment due to the large capital costs associated with polymer production.

low-cost supply and the competing cost for distributor profit. It is additionally complicated by small consumer’s need for technical assistance and the uneven ability of distributors to supply such service.

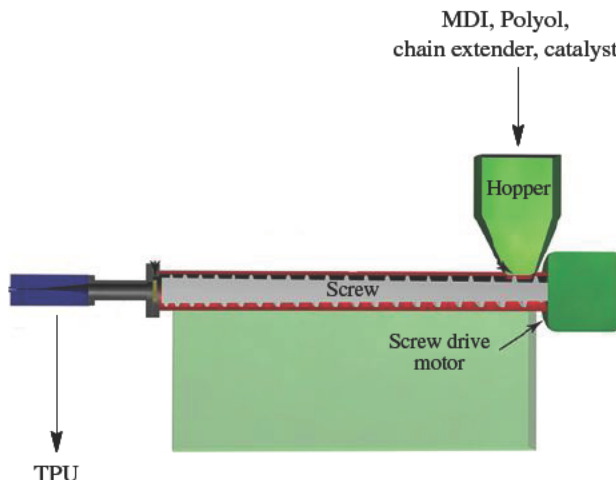


FIGURE 9.19 Simplified illustration of reactive extrusion of TPUs. Reprinted with permission from Ref. [46]. © John Wiley & Sons, Inc.

TPU technology is relatively straightforward and highly optimized. TPUs are produced by reactive extrusion in which all of the ingredients are simultaneously introduced to a twin-screw extruder, and under temperature and mixing action within the screw elements, produces a fully formed polymer at the extruder exit (Fig. 9.19). Almost all TPUs are made with MDI and butanediol for the hard segment. Soft segment differences have been the major area of differentiation in performance and price. The reaction is catalyzed using hydrolyzable tin catalysts such as tin octanoate. Hydrolytically stable catalysts such as dibutyl tin dilaurate are not used industrially to avoid complications of a live catalyst in the polymer for long periods. In the past, tin catalysts were preferred to amine catalysts because of lower color formation, lower odor, and specificity for the urethane reaction; however, recent restrictions, particularly in Europe, have generated increased reliance on amines [50].

While it is a simple matter to substitute TPU reactive components, most commercially available TPUs comprise MDI and BDO hard segments. Manufacturers will use different soft segments depending on the application. For hydrolytically sensitive applications, manufacturers will typically use polyether polyols. The vast majority of these use polytetramethylene ether glycol (PTMEG) that is prepared from the polymerization of THF (see Chapter 2). PTMEG has many good attributes contributing to TPU properties. Among these is that as a linear molecule, it is able to accommodate a balance of hard phase separation with hard phase dispersion. The phase separation is accommodated by PTMEG only interacting with hard segment by hydrogen bonding through the ether linkage [51, 52]. This limited soft segment–hard segment interaction minimizes the competition with hard segment–hard segment interaction. In addition, as an unbranched chain, PTMEG does not preferentially compete for free volume in the polymer, optimizing hard segment phase dispersion. Another benefit of PTMEG is that the terminal hydroxyls of PTMEG are all primary,

maximizing the reaction rate with isocyanates. PTMEG is also able to strain crystallize at higher molecular weights, and therefore increases the ultimate tensile strength of the polymer. Finally, due to the method of preparation (see Chapter 2), all the polymer chains in PTMEG are bifunctional maximizing network connectivity and elastomer properties. TPUs based on PTMEG are generally regarded as possessing a very good balance of properties but are among the most expensive due to the market price of PTMEG which is tied to the price of tetrahydrofuran as opposed to the less-expensive propylene oxide (see Chapter 2) and a more expensive process (see Chapter 2). PTMEG is a polyether, and therefore thermally limited by a relatively low ceiling temperature. At the ceiling temperature, the polymer will depolymerize back to starting materials—for polyethers usually between 230 and 250 °C [53].

Polyethers based on polypropylene oxide (PPO) make poorer TPUs than does PTMEG due to macrophase separation of hard segment caused by the free volume requirement of PPO pendant methyl groups [54]. Equally problematic for TPUs prepared from PPO is the slow reactivity of the terminal secondary hydroxyl groups of these soft segments. The reactivity ratio of secondary to primary hydroxyls is at least a factor of 3 (see Chapter 3), which makes it difficult to complete polymerization during the short reaction time in the reactive extruder, and also drives the equilibrium of hydroxyl and isocyanate to urethane unfavorably back to reactants [55]. Last, due to reaction isomerization, there is a net probability for some of the end groups of PPO to not create terminal hydroxyls, but instead create terminal allylic groups (see Chapter 2 for discussion of “monol” production). Since formation of allylic groups is a statistical process, and they are polymerization chain stoppers, their proportional importance is greater as soft segment molecular weight increases [56, 57].

TPUs prepared with polyethylene oxide soft segments are elastomeric, but phase separation of hard and soft segments is hindered by the large number of ether groups in the soft segment available to hydrogen bond with the hard segment [58, 59]. This hard–soft segment interaction competes with intrahard segment hydrogen bonding promoting *phase mixing* rather than phase segregation. In addition, polyethylene oxide soft segments are relatively hygroscopic. TPUs with polyethylene oxide absorb up to 15% of their weight in water from the atmosphere [60], whereas TPU with PTMEG soft segments will absorb about 1% water by mass at standard test conditions. Water plasticization of PEG TPUs greatly degrades TPU tensile properties.

TPUs are also commonly prepared with polyester soft segments. Polyester soft segments are preferred for applications where potential hydrolysis of the material is not an issue for long-term performance, and where cost is of paramount concern. Most polyester TPUs employ soft segments made from the condensation polymerization of adipic acid and butanediol. Along with a price that is less than half that of PTMEG, polyester polyol creates acceptable and transparent thermoplastic elastomers. Further, polyesters offer superior thermal stability to polyether polyols but can lose molecular weight in the presence of moisture and heat, reverting to reactant acids and alcohols. This degradation pathway can be catalyzed by the presence of acid end groups that are an inevitable artifact of the polyester polymerization. These acid end groups also degrade PU network connectivity by effectively acting as chain stoppers.

The carbonyl groups of polyester polyols are efficient competitors with urethane carbonyls for hydrogen bonding with the urethane N–H. The result of this is that a higher volume percentage of hard segment is required to affect hard segment–soft segment phase separation, and the equilibrium mixing of nonphase separated urethane groups is relatively high [61, 62] (see Chapter 4). This can result in a higher soft segment T_g in the polymer; however in many cases, this effect is not significant enough to greatly hinder low-temperature toughness of these materials.

With alternative thermoplastic elastomers available, the parts designer must try to evaluate the suitability of a particular material for its role. TPUs are conventionally considered very high-performing elastomers with a very good balance of properties, but not ideal for all applications. Table 9.11 shows comparative properties for TPUs from polyether and polyester soft segments compared with a generic block copolymer polyester elastomer and an olefin elastomer. While many properties are good for each elastomer class, there is no doubt that TPUs distinguish themselves with regard to tensile, dynamic, and abrasion dimensions of performance.

As mentioned earlier, it is a simple matter to prepare new TPU formulations as long as the materials can form a thermoplastic (all components are two functional), are dry, are matched stoichiometrically, and are properly catalyzed for reaction during their residence within the reactive extruder. Table 9.12 provides illustrative formulations for making TPUs of a given hardness. They are conveniently prepared

TABLE 9.11 Comparison of properties for typical thermoplastic elastomer classes

Property	Copolyester elastomer	Olefin elastomer	Polyether polyurethane	Polyester polyurethane
Transparency	0	+/0	+	+
Tensile strength	+	+/0	+	+
High temperature tensile properties	0	–	0	0
Modulus	+	0	+	+
Abrasion resistance	0	–	+	+
Compression set	0	–	+	+
Tensile set	0	–	+	+
Tear strength	+	+	+	+
Low temperature resilience	0	+	+	+
Chemical resistance	0	+	0	0
High temperature stability	0	–	+	+
Water resistance	–	+	–	+
Weather ability	+	+	+/-aliphatic/ aromatic	+/-aliphatic/ aromatic
Density	–	+	0	–
Cost	–	+	0	+

The choice of which elastomer to use will depend on performance and price requirements.

+ Indicates good performance.

0 Indicates adequate performance in limited situations.

– Indicates relatively poorer performance.

TABLE 9.12 Example formulations for TPUs of various hardnesses (modulus) and from various soft segments

Component	Shore A 70	Shore A 80	Shore A 91	Shore A 92
PTMEG 2000	72			
PTMEG 1000		60		
Polycaprolactone			60	
Polybutylene adipate				60
BDO	5	6.5	8.4	8.4
4,4' MDI	23	33.7	31.6	31.6
Modulus (psi)	450	770	1300	800
Elongation at break (%)	655	560	1700	2200
Break stress	4700	6800	5650	9000
Abrasion (mm ³)	37	33	27	35
T_g (°C)	-44	-25	-18	-14
Isocyanate index	1.02	1.02	1.02	1.02
% Hard segment	28	40	40	40

by their simultaneous introduction into the feed throat of a reactive extruder such as drawn in Figure 9.19. Along with the reactive components, the manufacturer will often introduce catalysts, antioxidants, processing aids such as waxes for easy transit through the process and mitigating interpellet stickiness, and also small amounts of monofunctional alcohols to limit molecular weight if a higher melt index polymer melt rheology is desired.

9.2.2.3 Reaction Injection Molding Elastomers Reaction injection molding (commonly referred to as “RIM”) is a processing technique for forming relatively large urethane elastomer structural panels. To provide adequate structural rigidity, it is common to incorporate glass or mineral fiber fillers into the polymer structure [63, 64]. As with all composites, process innovation has created numerous hyphenated forms of RIM. The basic process is superficially similar to that of some cast elastomer processes and thermoplastic injection molding. The components of the urethane matrix are energetically mixed and injected or poured into a mold. In many cases, the mold is prearranged with a glass fiber mat that provides composite reinforcement. Other embodiments may have the glass or other filler applied to the casting polymer solution and the mold subsequently closed. The details of the injection process and the composite phase employed are coded into the prefix used to identify the RIM species. For instance,

- **Reinforced RIM (R-RIM)**—This is the process in which short mineral fibers are dispersed into the polyol phase and mixed with the isocyanate phase prior to injecting the reacting mixture into a closed mold.
- **Structural-RIM [65] (S-RIM)**—This is the process in which prior to injection of the reacting mixture, the mold is prelaidd with a woven glass mat or prepreg. Usually, a closed mold but not required. This technique may also be termed LD-RIM for low-density RIM.

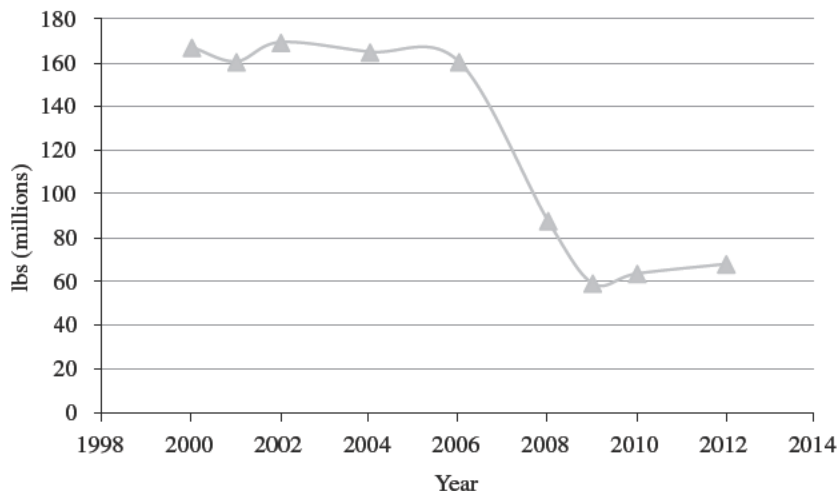


FIGURE 9.20 Volume production of polyurethane building blocks for RIM applications.

- LFI-PUR [66]—This is the process in which chopped long glass fiber is randomly applied to a mold simultaneously with the reacting polyurethane resin and the mold either left open or closed.

A pultrusion operation is yet another way of making a PU composite [67]. In a pultrusion operation, a fiberglass roving, yarn, or mat is drawn through a molten polymer or reactive system, and cured by continuous draw through an oven. The result is a material of constant cross-section. While often anisotropic in properties, unidirectionality can be offset by the use of off-axis fiber alignments.

Historically, the primary use of RIM PU products has been for automotive structures such as bumpers, vertical structural panels, and under-the-hood applications that are not in direct contact with the engine. However, the increasing use of formulated thermoplastic olefin elastomers (referred to as TPOs) has seen the utilization of RIM decrease dramatically (Fig. 9.20). The drop in RIM consumption reflects a significant drop in automotive production at that time. In the 1990s, there was a similar fall-off in RIM-based PU consumption due to the rapid adoption of the less-expensive, lighter, and less complex TPOs in the automotive industry. Other uses for RIM have remained approximately steady in terms of volumes including continued use in some automotive platforms, tractor panels, snowmobile panels, and furniture [68].

In terms of a competitive landscape for material solutions, PU composites can be compared with technologies employing epoxy matrices in resin transfer operations, or sheet molding compound (SMC) usually employing an unsaturated polyester resin. A qualitative comparison of properties obtained by these techniques is provided in Table 9.13 [69].

The processing conditions of a RIM part are as much a part of formulation conditions as final composite properties. The ability to rapidly and reliably produce high-quality parts at competitive costs will be implied in the choice of each component and how the overall system is employed (Table 9.14).

TABLE 9.13 Comparison of properties obtained for various plastic composites

	R-RIM	S-RIM	LFI-PU	RTM	SMC
Resin	PU	PU	PU	Epoxy	Polyester
Cycle time	Fast	Slow	Slow	Slow	Fast
Applicable to large parts?	No	No	Yes	Yes	Yes
Easily automated?	Yes	Partial	Yes	Partial	Yes
Surface quality ^a	Good	Good	Good	Good	Good
Modulus	Low	High	High	High	High
Toughness ^b	High	High	High	Low	Medium
Thermally stable?	Moderate	Moderate	Moderate	High	High

R-RIM is polyurethane reinforced with mineral fiber, S-RIM is polyurethane reinforced with glass mat, LFI-RIM is polyurethane reinforced with long chopped glass fiber, RTM is epoxy resin reinforced with a glass prepreg in a resin transfer molding operation, and SMC is a sheet molding compound of glass fiber reinforced with a polyester resin.

^aClass A or near class A obtainable.

^bDefined as the integral under a stress–strain curve.

TABLE 9.14 A modified S-RIM formulation that could be scaled for making an automotive door panel

Component	Weight	Comments
Polyether triblock polyol 85% PO/15% EO cap	34	Three functional 1600 equiv wt
Propoxylated ethylene diamine	50	Four functional 88 equiv wt
Ethylene glycol	14	Chain extender
Water	1.5	Chain extender/blowing agent
Silicone surfactant	1	
Pentamethyldiethylene triamine	1	
dimethylethanolamine	0.75	Reactive catalyst
Triethylene diamine	0.75	Gelation catalyst
Milled glass fiber	50	Avg 200m
Polymeric MDI (105 index)	175	2.7 functionality; 135 isocyanate equiv wt
Condition	Value	
Throughput	750 g/s	
Shot time	1.5 s	
Material temp	35 °C	
Mold temp	65–80 °C	
Air loading	30%	
Cure time	30–60 s	
Demold time	45 s	
Mold size	400×600×45 mm	
Property	Value	
Density	0.38 g/cm ³	
Flex modulus ^a	830 MPa	
Bending strength ^b	14.8 MPa	
Izod impact ^c	6 kJ/m ²	

^asee Chapter 10.

^b $= \frac{3PL}{wt^2}$ where P =break load, L =distance between bending fulcrums, w =sample width, t =sample thickness.

^cAccording to ASTM D256.

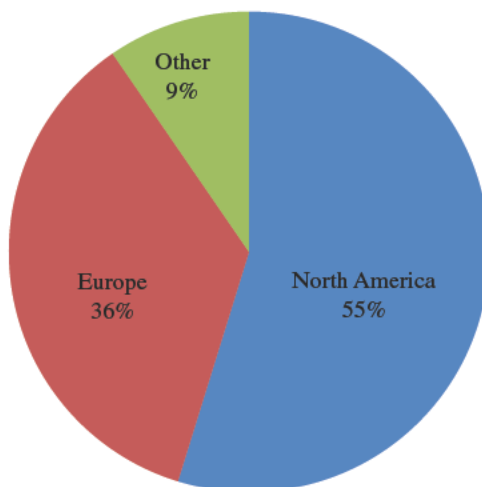


FIGURE 9.21 Geographical segmentation of RIM production in 2012.

The trends in RIM PUs are those mostly expressing the interests of manufacturers of RIM components rather than RIM consumers (Fig. 9.21). From 2008 through 2013, approximately 35 patents on RIM technology were filed. The subject matter of these patents varied widely but was primarily on the application of RIM to specific automotive parts. Although an average of about six patent filings a year is indicative of the general lack of commercial excitement in RIM technology, the most prevalent focus was on the application of RIM to automotive run-flat tires [70]. In nonautomotive applications, there were several patents filed on the application of RIM methods to making windmill components [71]. In terms of RIM methods, there is activity protecting methods of fabrication using chopped long fiber to make Class A finished body panels, and techniques to improve PU wetting of glass mat preforms in S-RIM operations [72]. In addition, there was a patent on the use of seed oil-derived polyols in RIM formulations [73].

9.2.2.4 PU Elastomer Fibers The global changes in the PU elastomeric fiber (referred to generically as “spandex” or “elastane” fibers) industry are emblematic of significant changes in overall global manufacturing, and PU manufacturing specifically. Figure 9.22 shows the rapid growth of spandex manufacturing in China coupled with the tailing off of spandex manufacturing in the United States [74]. The trend for Europe is nearly identical to that for the United States over this time period. The market consumption points to several trends. One is that the overall market for spandex fiber is very strong and usage is expanding into numerous areas of everyday life, including nearly all clothing segments, upholstery, disposable diapers, and medical garments. The growth of consumption was mirrored, and probably caused, by the growth in excess manufacturing capacity and concomitant price pressures. The worldwide manufacturing asset utilization was only about 73% in 2010 matching growth in Chinese production capacity, and at the beginning of an increased rate of consolidation in US and European capacity [75]. During the period of record

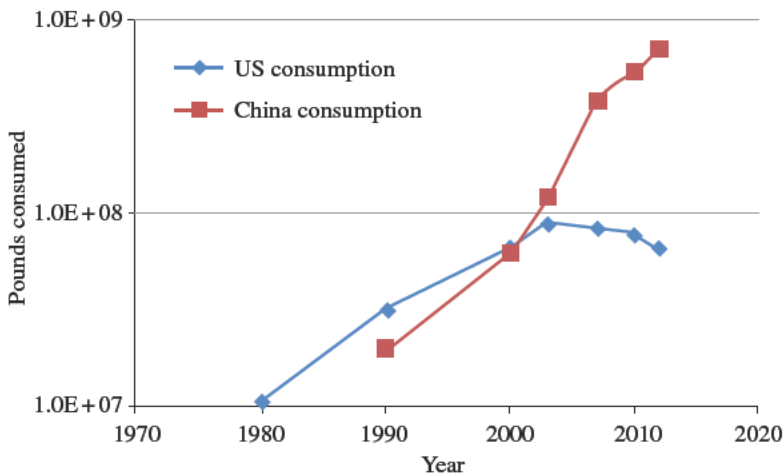


FIGURE 9.22 Industrial consumption of polyurethane elastomeric fiber.

for Figure 9.22, the price of spandex fibers went from a high of about \$22/kg in 1986 to a low of about \$5/kg in 2005. The fluctuating price of building blocks comprising spandex fibers, particularly PTMEG (see Chapter 2) has forced fiber price increases in the past few years. While it is assured that spandex prices will continue to fluctuate, the high prices of the 1980s are unlikely to be seen again. More recent prices have been in the \$8–10/kg range. A floor for spandex pricing is created by the costs of component building blocks and manufacturing costs.

Spandex fibers are technically PU-urea polymers employing diamine chain extenders, MDI, and either polyether or polyester soft segments. The need for polyurea hard segments is a result of the requirement for higher thermal stability than that offered by PU hard segments [76–78]. The need for elastomeric fabric stability in clothes dryers and under ironing conditions is critical in this regard. Further, due to the strength of *polyurea* hard segments, minimization of hard segment volume and maximization of soft segment volume in the polymer are achieved, creating a relatively soft polymer with very good elastomer retractive properties. Equivalent soft segment retracting power would require a larger amount of PU hard segment and result in an overall harder fiber that might reduce the comfort goal that these fibers have.

Production of spandex fibers is via a solution dry spinning process using a prepolymer route [79]. The producers manufacture the prepolymer by reacting the polyols with an excess of MDI (virtually all PU elastomeric fibers are made with 4,4' MDI) (Fig. 9.23). The amount of excess MDI is controlled to minimize chain extension whereby soft segment chains are polymerized with MDI, but not so much that too much hard segment is produced in the next step.

The prepolymer is subsequently dissolved in an aprotic polar solvent, usually dimethylformamide, and reacted with a diamine such as ethylene diamine (Fig. 9.24). The dilute (but still very viscous) solution is subsequently spun through a spinneret into a long heated shroud able to remove the significant amount of solvent involved,

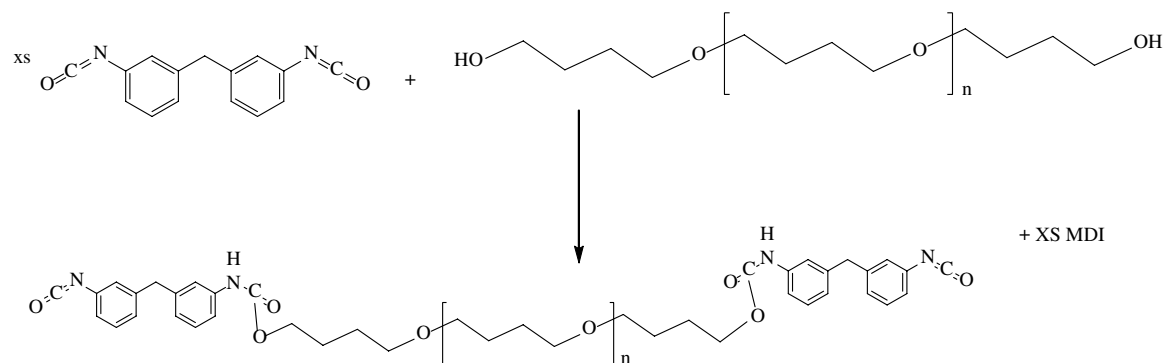


FIGURE 9.23 Synthesis of the prepolymer for making spandex. The soft segment shown is polytetramethylene glycol. Manufacturers may use polyester soft segments, although these potentially suffer from hydrolytic instability.

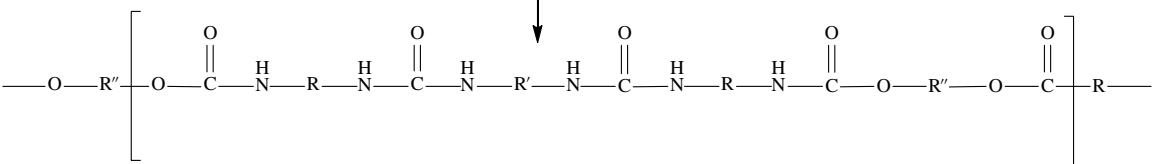
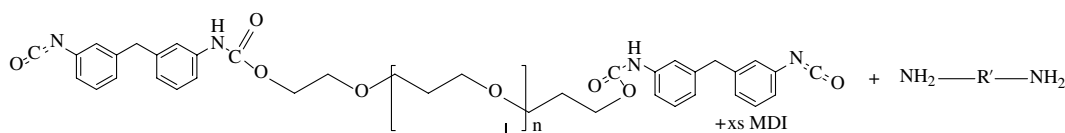


FIGURE 9.24 Preparation of spandex polyurethane urea polymer from prepolymer and diamine. R=methylene bisphenyl from MDI R' is a linear moiety-like ethylene form ethylene diamine, and R'' is the PTMEG soft segment. Reprinted with permission from Ref. [46]. © John Wiley and Sons, Inc.

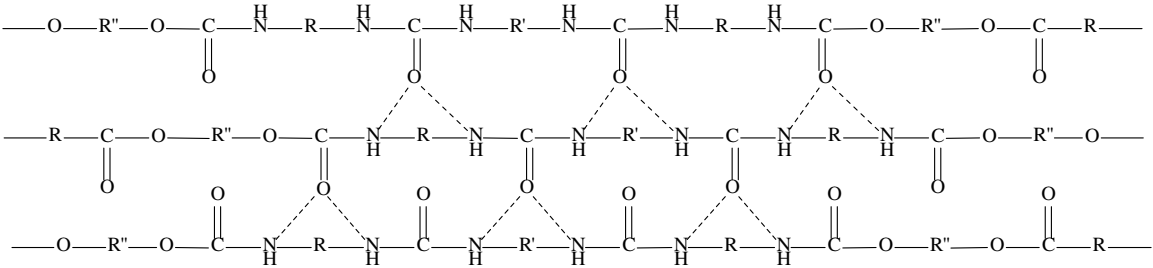


FIGURE 9.25 Hard segment structure stabilization through germinal hydrogen bond interaction between hard segments on different chains. Reprinted with permission from Ref. [46]. © John Wiley and Sons, Inc.

and leave the elastomeric fiber. The resulting polymer has a high density of interactive N–H units and carbonyl units that are capable of interchain interactions. The isocyanate-diamine hard segment phase separates from the soft segment by virtue of phase incompatibility (see Chapter 4), and hydrogen bond interaction between the N–H and carbonyls. The short distance between amine functions on a chain extender such as ethylene diamine allows for the unpaired electrons of carbonyl groups to simultaneously entertain two hydrogen bonds from the urea moiety. Thus, the intrachain cohesive energy between urea hard segments are as much as 2X that of urethane hard segments, and allows for stronger hard segment interactions allowing less hard segment volume for the same crosslink strength [80]. However, the high cohesive energy density of these hydrogen bonds precludes melt spinning of these materials due to decomposition of polyether soft segments at temperatures below the polyurea hard segment melting point (Fig. 9.25). The phase-separated urea segments act as crosslinks tying the soft segments together. From this standpoint, PU elastomers behavior is well understood by simple applications of the concepts of rubber elasticity.

A trend in spandex technology, besides lower cost, is to produce designed fibers that fill performance gaps in current spandex performance. Particularly, there is effort to produce spandex fibers that show less susceptibility to degradation upon exposure to chlorine. Chlorine exposure is known to greatly reduce the overall strength of elastomer fibers via a substitution of Cl for the carbamate hydrogen followed by eventual scission of the urethane bond, or by substitution for hydrogen along the polyether soft segment. Recently, major spandex producers have come forward with mineral-containing fibers improving chlorine resistance [81, 82]. Similarly, there is a push for fiber manufacturers to produce fibers compatible with various wrinkle-free technologies. Another trend is to produce commercial quality elastomeric fibers via a melt-spinning process (i.e. solvent-free) and therefore avoid the cost of solvent, solvent recovery, and environmental, health and safety concerns associated with a spinning solvent [83, 84]. As noted before, PU hard segments suffer from relatively poor thermal stability in comparison with polyurea hard segments, and require more hard segment volume in the polymer to achieve similar properties reducing overall elasticity in the fiber. Nevertheless, melt-spun fiber has been able to make some inroads into the market, primarily in the lower cost/lower performance segment of the market.

9.3 TRENDS IN PU ELASTOMERS

While the patent literature is notably poor at providing insight of fundamental science, it is the clearest way of understanding the future of a technology and market. This is because the patent literature represents a sizable investment by a company or individual on what is believed will be desirable by customers and market competitors in the next generation product. Further, defense of a patent asset requires that the technology on which a patent is based must be protected by patent prior to its commercial introduction.

While a single patent may not be instructive as to the direction of future innovation, a clear trend in industrial patent activity can be unmistakable. Worldwide, over 1650

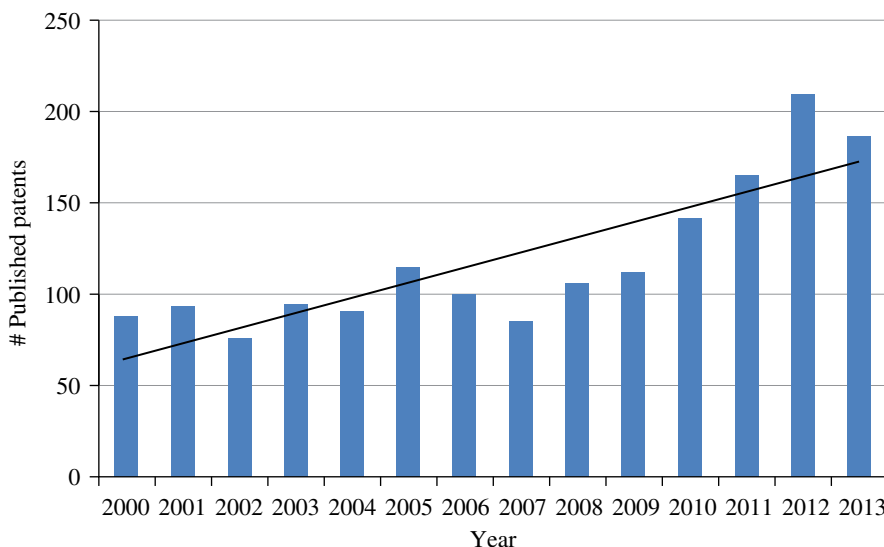


FIGURE 9.26 Trend of increasing published patents on polyurethane elastomers since 2000. There were 1660 total patents published worldwide over this period.

patents were granted on the subject of PU elastomers from 2000 to 2013. Figure 9.26 shows increasing patent activity from those years reflecting the increasing production and application areas for PU elastomers. Figure 9.27 shows an interesting geographical migration from Japan to China in PU elastomer patenting activity following the increasing production of raw materials and manufactured goods and intensification of competition among global participants. The bar graphs are in no way inclusive, and Figure 9.28 shows a pie chart of the number of patenting companies relative to the share patented by the top five companies from the years 2010 to 2013.

The topics for patent for the years 2000–2013 are shown in Figure 9.29. The greatest patent intensity is on the application of PU elastomers to specific market segments (rather than, for instance, production techniques or new compositions). Some of the categories shown in Figure 9.29 could rationally be combined such as plastic foams/shoes, nonwoven fabrics/textiles, golf balls/sporting goods, and so on, but are left uncollected for the cases when they are not in fact redundant. Another example would be crosslinking agents, which would probably, at least in part, overlap with textiles and fibers due to the use of crosslinking agents to impart wrinkle-free characteristics to cotton fabrics under challenging conditions for PU bonds. The data suggest that while there is some industrial application–patent activity such as for various conveyor rollers and abrasion resistant compositions, the majority of activity protects final user applications such as for clothing (including shoes), and sporting goods including golf balls and roller blade wheels. This analysis suggests that current research can be best applied to satisfying the needs of the consumers/leisure economy and applications that do not bring a tangible value to the end-user may have less long-term value.

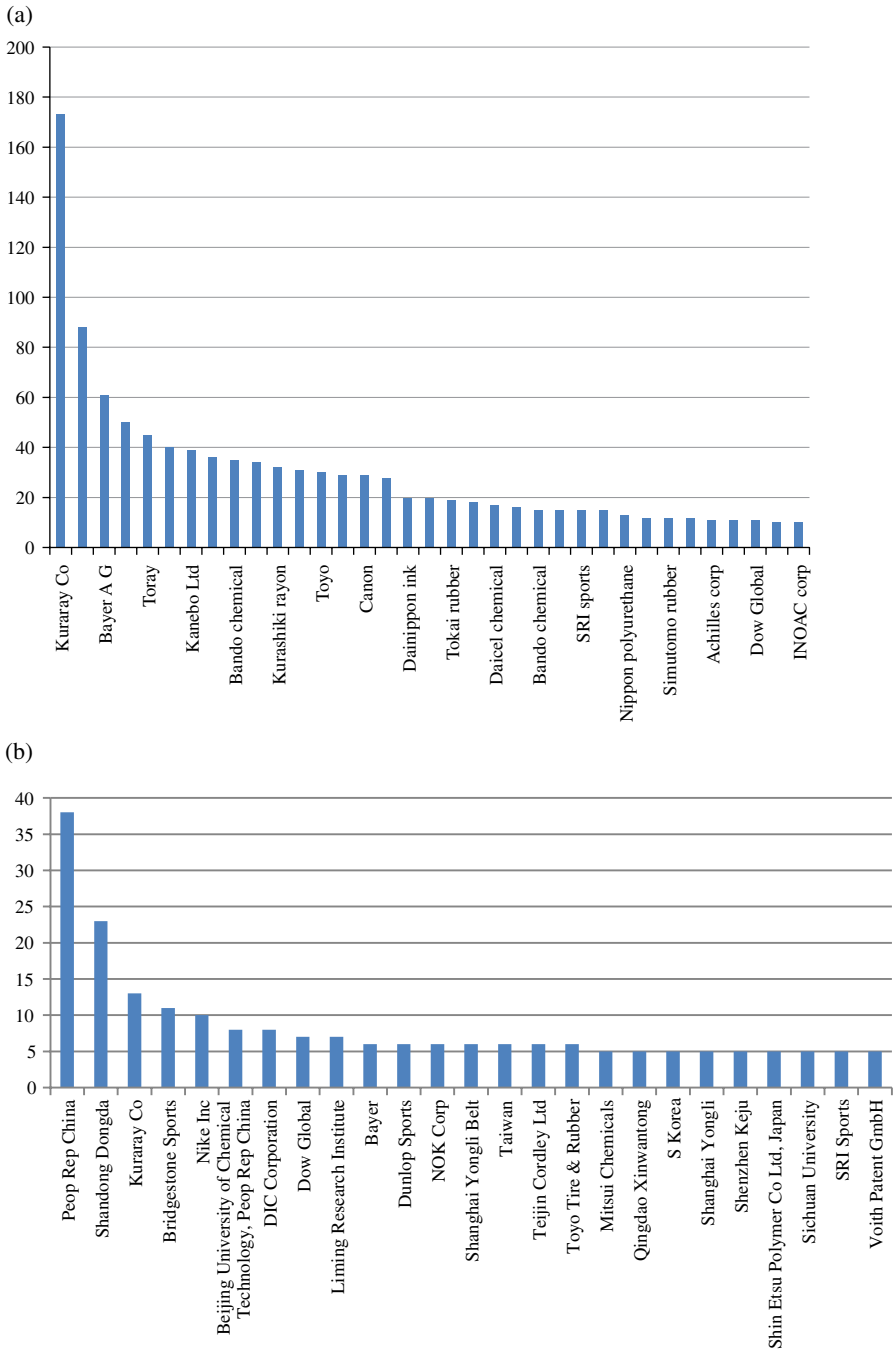


FIGURE 9.27 (a) Patent activity of companies from 2000 to 2010 with those having at least 10 patents. (b) Patent activity of companies from 2010 to 2013 with those having at least five patents. About 700 patents were published between 2010 and 2013.

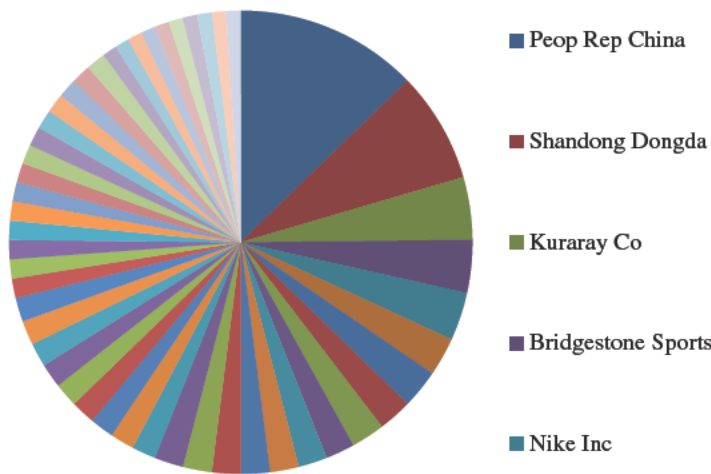


FIGURE 9.28 Pie chart of all patents filed from 2010 to 2013 relative to the activity of the top five assignees. The top five account for about 25% of all polyurethane elastomer patents filed. (See insert for color representation of the figure.)

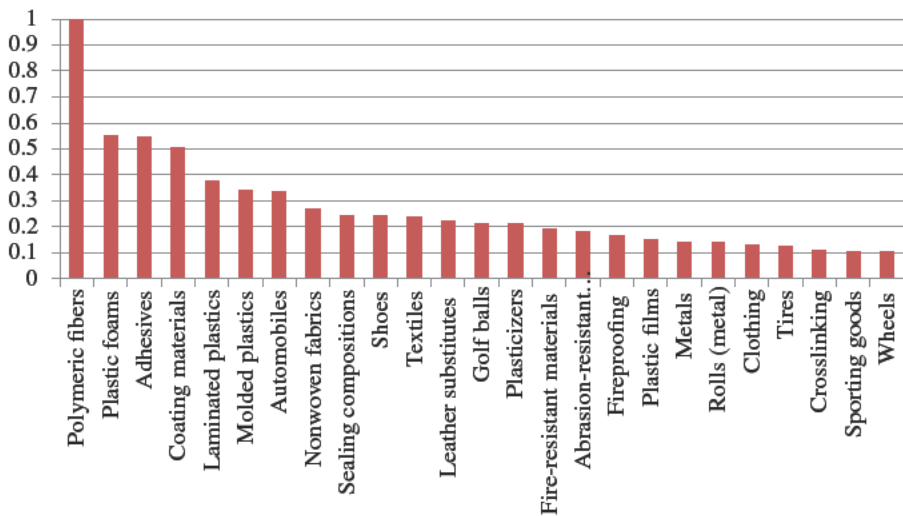


FIGURE 9.29 Normalized patent activity based on application of polyurethane elastomers.

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10

POLYURETHANE ADHESIVES AND COATINGS: MANUFACTURE, APPLICATIONS, MARKETS, AND TRENDS

10.1 ADHESIVE AND COATING INDUSTRIES: SIMILARITIES AND DIFFERENCES

Coatings and adhesives are commonly associated in polyurethane (PU) technology due to the commonality of how systems are manufactured and many of the technology trends. In both cases, a film must be applied to a surface, wet the surface, form an integral film, and adhere to the surface. In terms of raw material, applications, and markets, they are as different as people commonly understand their separate uses. More so than any other PU-based technology, coatings and adhesives are formulated systems of which the PU may represent a significant volume, but is often serving as a binder for all the other components put into the system. These additional components are often things such as solvents, solid fillers, pigments and dyes, antioxidants, tougheners, surfactants, coupling agents, coalescing agents, catalysts, defoamers, moisture scavengers, water, plasticizers, and numerous hybridizing polymers.

The technologies for producing both adhesives and coatings can be simplified into variations of reactive and unreactive systems (Fig. 10.1). The ratio of PU sold into the two markets is roughly 2:1 (Fig. 10.2). The market position of PU adhesives, sealants, and coatings is important to their overall industries, but they are by no means volume leaders (Fig. 10.3) [1–6].

Because of the highly formulated and often diluted nature of adhesive and coating products, it is challenging to obtain an accurate measure of total PU consumption for

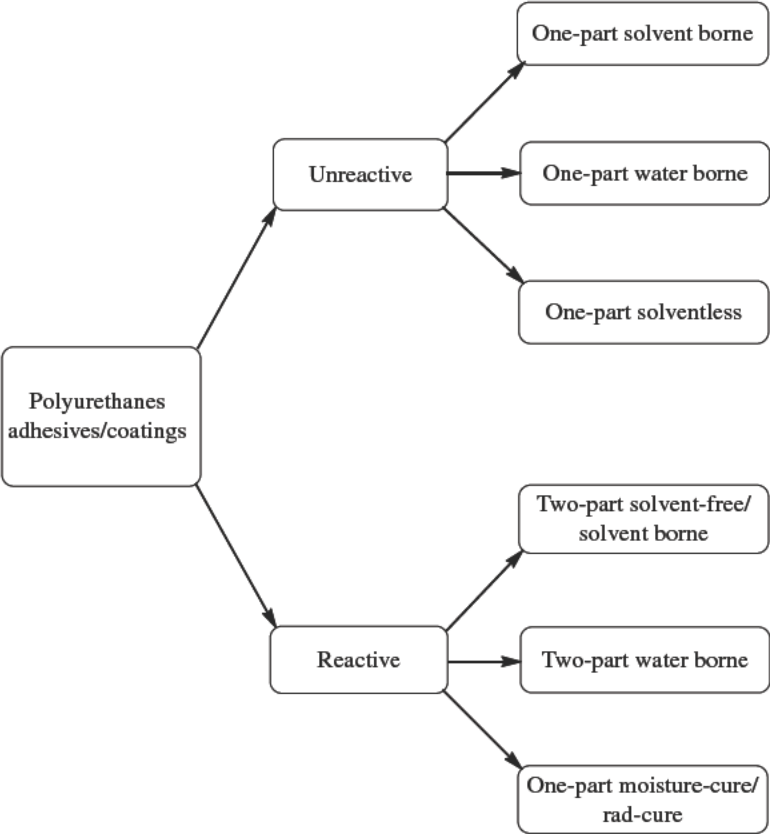


FIGURE 10.1 Technology structure of polyurethane coatings and adhesives by format. This commonality of product offerings is the reason for grouping these technologies.

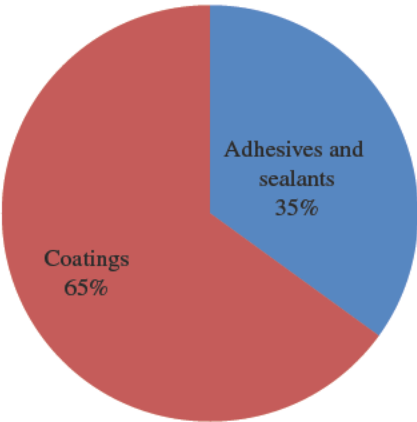


FIGURE 10.2 Relative volume of polyurethane used in adhesive and sealants versus coatings.

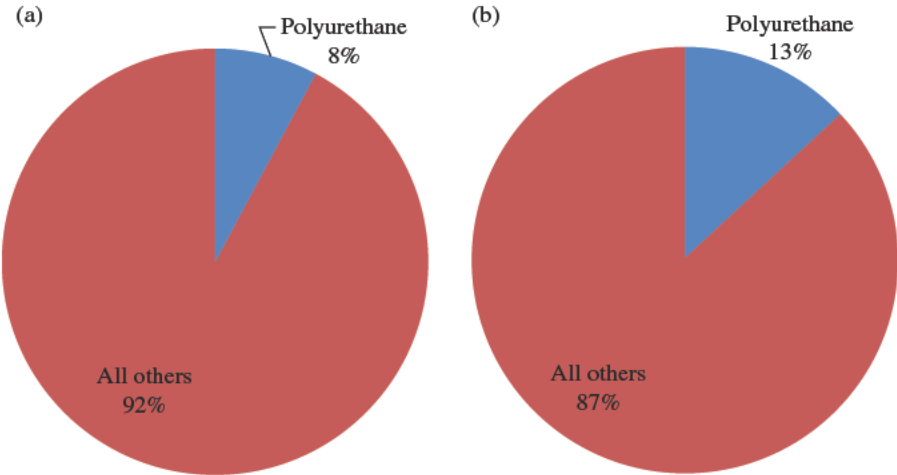


FIGURE 10.3 Relative market position of polyurethane in (a) adhesives and sealants market and (b) coatings market. Percentages are based on dry volume.

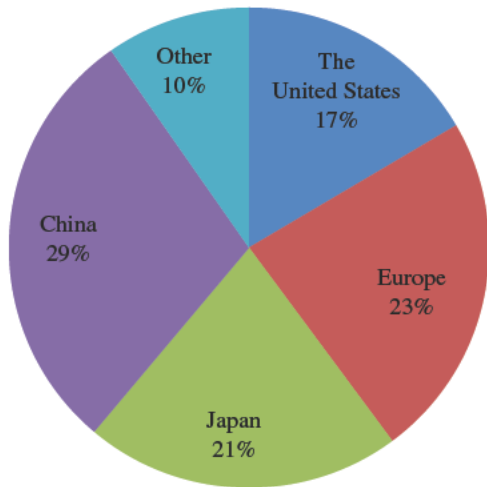


FIGURE 10.4 Distribution of global consumption of polyurethane coatings by region.

these technologies. An analysis of the available market literature suggests that PU represents about 7–8% of all adhesive and sealant binders used with about a total of 800–900 million pounds used globally. Between the years 2005 and 2012, the annual growth rate was about 1% by volume. The coatings market accounts for about 1.5 billion pounds of PU consumption. For adhesives and sealants, the major markets are in order: construction>packaging>transportation>furniture>footwear.

Consumption of PU coatings is global and reflective of finished goods manufacturing that use PU coatings (Fig. 10.4). The global uniformity of consumption reflects

the convolution of industrial, architectural, and protective applications that use PU coatings. The prominence of Japan's consumption reflects the use of PU coatings in automotive assembly and architectural coatings in that order.

There are numerous applications consuming similar volume including automotive coatings, wood coatings, artificial leathers, and protective industrial coatings. This versatility is in part responsible for the global breadth of PU that does not favor consumption based on any single manufacturing center. Further, because of highly formulated and customized solutions, each particular customer requires local technical service and production, again favoring a broad distribution of geographical consumption. For this reason, the general appearance of geographical consumption of PU adhesives would have a qualitatively similar appearance to Figure 10.4 with a smaller participation by Japan and a larger participation by the rest of the world.

The similarities in product format and global utilization belie the very different uses of adhesives and coatings and the resulting needs for specific polymer design and requirements [7–9]. In Sections, 10.2 and 10.3, adhesives and coatings will be treated separately to more fully reflect this reality.

10.2 ADHESIVES

As indicated in Figure 10.1, PU adhesives are commercialized in numerous product forms. Each form exists because it caters to the needs of particular industries and customers. The particular technology used bespeaks the mode of adhesive action and the requirements of the application. The global use of formulated PU adhesives according to product form is shown in Figure 10.5.

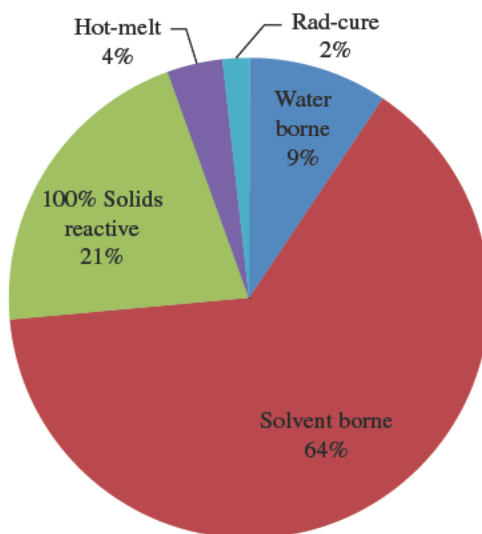


FIGURE 10.5 Global consumption of polyurethane adhesives by total formulated product.

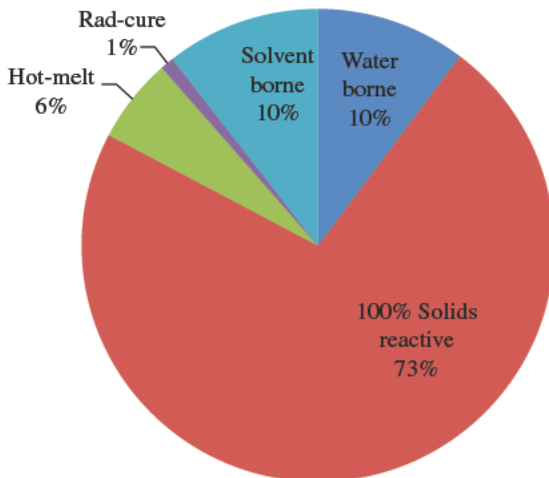


FIGURE 10.6 Global consumption of polyurethane in polyurethane adhesives.

Of course, the fully formulated product is weighted by the accompanying formulation components that, in the case of solvent-borne adhesives for instance, can actually outweigh the PU polymer component. The distribution representing only the binder component looks quite different (Fig. 10.6).

The large volume of solvent-borne PU adhesive reflects the very large volumes applied for shoe sole construction. This is particularly evident in PU adhesive consumption in China where footwear manufacturing is dominant and estimated 80% of solvent-borne PU adhesive is consumed [1]. The geographical distribution of adhesive consumption by format is complex and changing based on downstream manufacturing. Due to the specialty and customer-specific nature of the applications, the adhesive producers are located close to the assembly operations that utilize the particular adhesive. As manufacturers of finished goods move to more favorable geographies, the adhesive supply and portfolio of adhesive solutions tend to follow.

The large chemical producers supply the adhesive formulators with the typical building blocks used for other PU applications. Due to economic advantage brought by their back integration, most of these large chemical producers have a significant adhesive product offering, either as fully formulated systems, or via component sales to small and large adhesive producers. This situation can result in these companies being in direct competition with their customers in some markets.

While many small formulators have minimal technical capabilities beyond blending and packaging, other formulators are technically sophisticated, highly capable, and well known. Consumers of building blocks for adhesives face the same commercial challenges and must choose from similar building blocks to develop adhesive solutions. The result of this constant evolution has resulted in methylene diphenyl diisocyanate (MDI) and polymeric MDI (pMDI) enjoying approximately three-fourth of the overall PU market for adhesives, and polyethers dominating polyester soft segment volumes by 4:1 (Fig. 10.7). The dominance of MDI/pMDI for

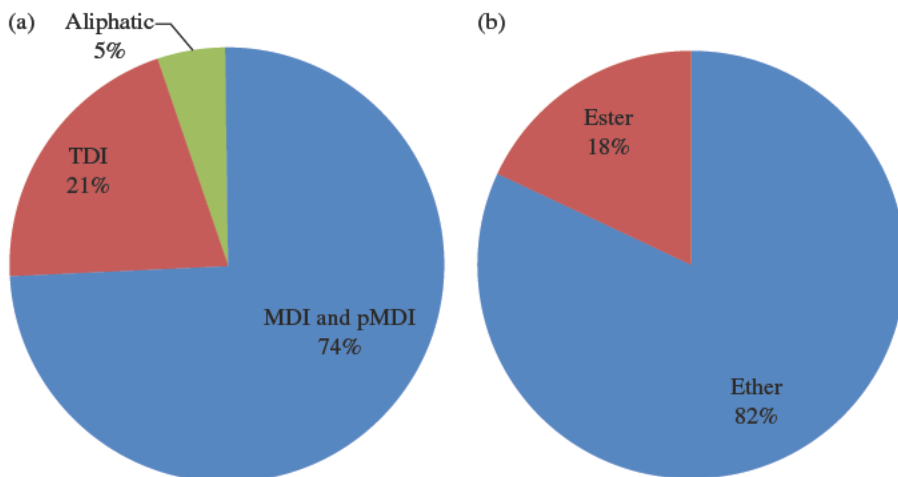


FIGURE 10.7 Global consumption of (a) isocyanates and (b) polyols for polyurethane adhesives formulation.

adhesives reflects the uniform reactivity of the isocyanate groups, low volatility resulting in easier workplace handling, and the fact that most adhesives do not require specific inhibition from light-stimulated degradation such as required for coatings. Coatings exposed to degrading light require an aliphatic isocyanate rather than less-expensive aromatic isocyanate. The dominance of polyether polyols reflects that they are room temperature liquids, offer superior low-temperature flexibility, and are much less sensitive to hydrolysis than polyesters. Polyesters are more common in applications requiring faster set times or initial green strength such as required for some hotmelt adhesives, and highly automated high unit volume applications.

Table 10.1 lists the various PU adhesive formats and representative associated applications. Some of the different formats may be used for the same application and may find favor with specific manufacturers based on customer requirements, environmental–health–safety goals of the manufacturer, and preference of the manufacturer. There has been a general move toward waterborne formulations as manufacturers attempt to reduce the volatile organic compounds (VOCs) in their workplace and customer venues [10–12]. Another characteristic of these categories is that two-part adhesives are higher performing than a corresponding one-part adhesives in terms of thermal and solvent resistance because of the ability to build hard segment volume [13]. The growth of *reactive* PU hotmelts is recognition of their ability to generate lower viscosity at elevated temperatures, obtain excellent cohesive and adhesive strength as full cure is achieved, and the attractive properties of PU backbones are fully realized [14, 15]. Thus, the bookbinding application has particularly been able to generate customers for reactive hotmelts due to the long-term durability and flexibility of the product.

The large number of adhesive formats, substrates, applications, and application techniques has resulted in high reliance on standardized test methods to facilitate

TABLE 10.1 Major applications for polyurethane adhesives as a function of format

Adhesive format	Applications
One-part solvent-borne	Food packaging and footwear May include blocked isocyanates requiring elevated temperature curing
One-part waterborne	Footwear, bookbinding, fiberglass sizing and textile laminates
One-part solventless	Hotmelt—book bindings, furniture, apparel, pMDI wood bonding, and food packaging
Two-part solvent-free/ solvent-borne	Same as one-part but offering improved properties, flexible packaging, footwear, interlayer laminates for windows, flooring, and metal-to-plastic bonding (often requires a primer)
Two-part waterborne	Wood bonding, automotive dashboards and instrument panel linings, footwear, lamination of veneers and films for furniture, and exterior sandwich panels for construction
One-part moisture cure/rad cure	Reactive hotmelt for packaging, furniture, bookbinding and wooden flooring Moisture cure-automotive windshield Rad-cure (acrylate tipped) tougheners and structural adhesives

comparisons of adhesives and adhesion. A representative list of standardized test methods is provided in Table 10.2 [16]. Along with the standardized tests, it is also commonplace for industrial adhesive consumers to perform nonstandardized application testing, or to demand the same of their suppliers. Many of the tests lay emphasis on sample preparation, test geometry, and conditions, due to difficulty separating factors associated with overall adhesive performance. The large number of controls can help differentiate confusing variables that can mislead the designer from determining true performance.

The measure of adhesion using standards proscribed in Table 10.2 are the final result of interfacial and rheological forces PUs offer in building a joined system. PUs function well due to their high internal cohesive strength within the adhesive layer, as a result of its block copolymer structure and internal hydrogen bonding. The same polymer material properties contribute to strong interfacial adhesives resulting from the same strong polar and hydrogen bonding interactions. In addition, reactive PU adhesives have the potential to chemically bond across the interface with substrates that offer active hydrogens on the surface. Detailed discussions of the specifics of adhesion and adhesives is available from numerous excellent source books devoted to the subject [17, 18].

10.2.1 Adhesive Formulations

10.2.1.1 One-Part Adhesives There is a general industrial move away from application of solvent-borne PU adhesives, but they retain high utility, particularly in the shoe sole market. The one-part adhesive is essentially a thermoplastic PU (TPU) dissolved in a solvent. The solvated TPU is applied to the prepared surface as a contact cement, or is applied, allowed to dry, and then adhesion generated by

TABLE 10.2 ASTM standard methods for testing adhesives

Test	Standard description
ASTM D4896	Standard test for performance of adhesion test in a single lap-shear geometry—one of the most common tests and also one of the most difficult to perform for unambiguous data
ASTM D1876	Standard test for adhesion in a T-peel geometry. Primarily used for flexible substrates requiring flexible adhesive such as PU. See also D2919.
ASTM D1144	Standard test for determining strength development of adhesive bonds. This test is particularly relevant to PU-reactive adhesives that require days to weeks to develop full adhesion and adhesive strength.
ASTM D905	Standard test method for strength properties of adhesive bonds in shear by compressive loading. Applies specifically to wood substrates for which PU adhesives are highly employed. Standard is very specific about all aspects of test.
ASTM D950	Standard test method for impact strength of adhesive bonds. Uses a pendulum impactor on substrates in a shear geometry with a standard velocity of 3.4 m/s (7.6 mph).
ASTM D897	Standard test method for tensile properties of adhesive bonds. Utilizes metal substrates and a strain rate of 0.05 in/min.
ASTM D1151	Standard practice for effect of moisture and temperature on adhesive bonds. Continuous exposure test for samples exposed to conditions from -57 to 316°C and from 50% humidity to saturated by soaking. Samples at high-temperature conditions are aged in oven with uncontrolled humidity.
ASTM D7105	Standard test method for determining the adhesive and cohesive strength between materials in roofing or waterproofing membranes and systems. These are applications for which PU adhesives are commonly applied.
ASTM D896	Standard practice for resistance of adhesive bonds to chemical reagents. Quantification of adhesive performance following chemical exposure is a requirement for many applications.
ASTM D4501	Standard test method for shear strength of adhesive bonds between rigid substrates by the block shear method. Specific to substrates with higher modulus than the adhesive and where machining of the substrate is impractical such as with glass bonding—a common substrate for PU adhesives for windshield adhesive/sealants.
ASTM D3930	Standard specification for adhesives for wood-based materials for construction of manufactured homes. Comprehensive standard for application commonly employing polyurethane adhesives.
ASTM D1337	Standard practice for storage life of adhesives by viscosity and bond strength. A common qualifying attribute for all adhesives including polyurethanes.
ASTM C1523	Standard test method for determining modulus, tear, and adhesion properties of procured elastomeric joint sealants
ASTM D3433	Standard test method for fracture strength in cleavage of adhesives in bonded metal joints. Specifies metal but is applicable to all stiff adherends using structural adhesives not prone to elastic deformation. Employs a dual cantilever beam geometry.
ASTM D 4497	Standard test method for determining the open time of hotmelt adhesives. Very simple manual test.
ASTM D 4498	Standard test method for heat-fail temperature in shear of hotmelt adhesives. A common test for hotmelt adhesive performance.

TABLE 10.3 Example formulation and properties of a one-part solvent-borne polyurethane adhesive

TPU component	pphp
3000 mwt polybutylene adipate	16
Butane diol	0.42
4,4' MDI	3.58
Methyl ethyl ketone	80
Properties	
Viscosity (25 °C)	2000 cps
T_g	-000
Engineering strain at break (of adhesive film)	1200%
Tensile strength (of adhesive film)	30 MPa
90°T-peel (polyurethane to leather)	30 lbs/linear-in

contacting the adherends with heat. The adhesive designer will design the system to meet the performance and process requirements of the application [19].

Although polyether soft segments dominate the adhesive application, many one-component solvent-borne PU adhesives will employ a polyester soft segment such as polybutylene adipate for the simple reason that its ability to crystallize can increase the initial adhesion between adherends [20]. A typical formulation is suggested in Table 10.3. The TPU would normally be polymerized in a separate operation and then dissolved in the adhesive solvent. It is noticeable that the TPU has a relatively low hard segment fraction, about 25%, and that the hard segment length (BDO/PBA) is approximately 1. This assures that the resulting adhesive will have a low glass transition temperature for good performance at low temperatures, and also that the adhesive will possess very good flexibility. If the designer determines that the process requires more rapid buildup of adhesion properties, hexanediol could be substituted for butanediol in the soft segment. It is known that for systems that use one-part solvent-borne PU adhesives, pretreatment of the surface can be critical to performance [21]. This can involve extensive roughening of the surfaces to be joined, and also the use of a primer coating that has preferential adhesion to the substrate and the TPU, but does not possess sufficient properties as a sole adhesive layer to function in the application [22]. Typical primer polymers are substances such as chlorinated polyethylene at high dilution in an aromatic solvent such as toluene. For these systems, the solvent can also be a major participant in the growth of adhesion by swelling both the substrate and the adhesive polymers to promote polymer chain entanglement or physical interlocking of larger polymer segments that form as the adhesive laminate swells and then contracts [23, 24].

A two-part solvent-borne version of PU adhesives is typically an isocyanate-tipped prepolymer with relatively low isocyanate content (5–12%) on the one side, and chain extender (diol or diamine), catalyst, and often a cross-linker for the second component. A two-part solvent-borne system has the benefit of allowing the opportunity to tune adhesive modulus and improve solvent resistance via the cross-linking capability. However; beyond the obvious problem with VOCs, this format suffers

from the complication of properties being dependent on accurate weighing of the adhesive parts, and also the unavoidable limitations on open time that come from a reacting system. In addition, PU side reactions, particularly with ambient water, are capable of producing CO_2 gas. In the limit of high humidity, this can have the very undesirable effect of foaming the adhesive layer. A merge of one-part and two-part adhesive technologies is achieved by combining all PU components into a single solvent system but employing a blocked isocyanate. Blocked isocyanates are standard polyisocyanates prereacted with weakly bonded active hydrogen groups. When heated, the weakly reacted components decouple releasing the original polyisocyanate and the blocking agent. This technology of course requires that the bonded substrates be heated under compression to effect the desired polymerization and bonding chemistry (see Section 10.3.1.5).

10.2.1.2 Hotmelt Adhesives

Nonreactive Hotmelt Adhesive Hotmelt adhesives are thermoplastic materials that (i) are heated and applied to a substrate in the molten state, (ii) the bonding substrates are assembled, and (iii) the thermoplastic resolidifies back to its thermoplastic state. If the substrate is wet by the adhesive, if the polar interactions across the adhesive–substrate interface are of sufficient number and strength, and if the adhesive has adequate cohesive energy, a durable bond can be established. TPUs have been employed for this application and have a market appeal, particularly for wood bonding and shoe sole operations. Polyester polyols are often used in these applications since crystallization of the soft segment can speed up TPU resolidification and therefore increase the rate of adhesive strength build. Simple TPU hotmelt adhesives usually suffer in performance comparison to high-performance polyamide and polyester hotmelt adhesives. This is ascribed to the higher viscosity of TPU at standard application gun temperatures that limit substrate wetting. It is possible to reduce viscosity and thereby improve hotmelt adhesive properties by addition of a monol (e.g., replacing some amount of butanediol with 1-butanol). Substitution of even 5% of the butanediol chain extender with 1-butanol can reduce molecular weight of the chain limited polymer by a factor of 2–3 and reduce the viscosity of the polymer melt by over an order of magnitude based on the $\alpha \text{ Mn}^{3.5}$ rule [25]. This also can slightly reduce the overall polymer tensile performance by reducing hard segment formation and phase separation. An example of a PU hotmelt based on this design is provided in Table 10.4. The measures of quality for a hotmelt adhesive are unique to the technology reflecting viscosity of a polymer melt, and creep properties under a shear load. In addition, it is common to characterize the strength build of a hotmelt adhesive referred to as its “green strength” and its glass transition temperature.

Reactive Hotmelt Adhesive Reactive PU hotmelt adhesives are a technology introduced in the 1990s [26, 27]. It is essentially a low-percentage isocyanate prepolymer that is applied to a substrate and allowed to cure by reaction via adventitious moisture, or by direct reaction with substrates possessing active hydrogen on their surface. Reactive hotmelts possess a highly desirable grouping of properties including low viscosity at application temperatures, rapid generation of green strength when using

TABLE 10.4 Formulation and properties of a nonreactive polyurethane hotmelt adhesive

Component	pphp
Polycaprolactone $M_n = 530$	29.5
1,4-butane diol	14.24
1-butanol	0.62
4,4' MDI	55.64
viscosity at 190 °C	10,000 cps
Melt index 44 psi at 190 °C	160
T _g	0 °C
modulus of adhesive film	4.3×10^7 Pa/cm ²
elongation at break	500%
180°T-peel adhesion (canvas to Al)	9 pli
shear fail temperature	160 °C at 2 lbs/in ² stress 106 °C at 14 lbs/in ² stress

TABLE 10.5 Formulation and properties of a reactive polyurethane hotmelt adhesive

Component	Grams
4000 molecular weight polycaprolactone	100.0
50/50 o,p' MDI	14.62
Properties	
Viscosity at 121 °C/155 s ⁻¹	72 cps (shear thinning)
T _g (of the prepolymer)	56 °C
Open time	>2 min
Green strength at 2/15/30 min	0/5.4/6.8 lbs/linear-in
ASTM D6746	
Green strength at 2/7 days	32/>500 lbs

crystalizable soft segments, gradual development of very strong adhesive bonding, no VOCs, and the excellent material properties of PU elastomers. These properties and performance have made PU reactive hotmelts very competitive with polyamide and polyester hotmelts, and allowed this PU adhesive class to grow at twice the rate of PU s as a whole [2]. Prepolymers and their preparation are covered in Chapters 2 and 9. Table 10.5 provides the composition and properties of a 4000 g/mol polycaprolactone-based MDI prepolymer with 2.3% isocyanate useable as a reactive PU hotmelt adhesive. Polyether polyols can also be used to make very good reactive hotmelt adhesives, especially when the prepolymers are made of blended molecular weights to provide the mix of low viscosity and rapid green strength build.

10.2.1.3 Waterborne PU Adhesives Waterborne-PU dispersions (PUDs) have been an area of considerable interest and commercial growth since the first documented PUD in 1961 at E.I. DuPont de Nemours and Company [28]. The growth as measured by patent activity has been exponential beginning in the mid 1970s (Fig. 10.8). This

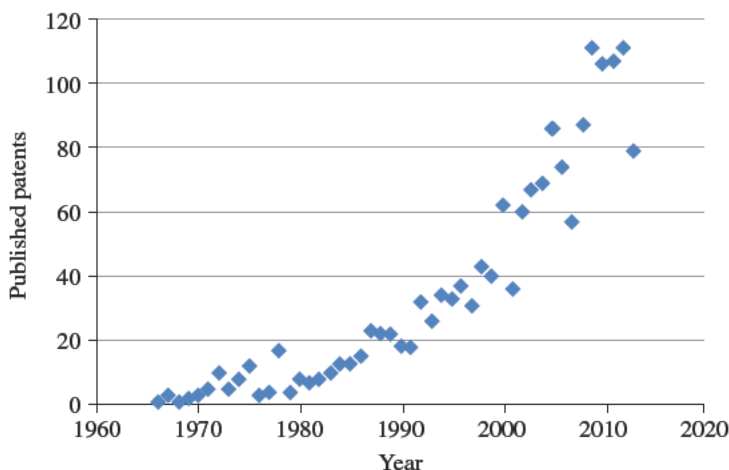


FIGURE 10.8 Growth in polyurethane dispersion patent activity since development in early 1960s.

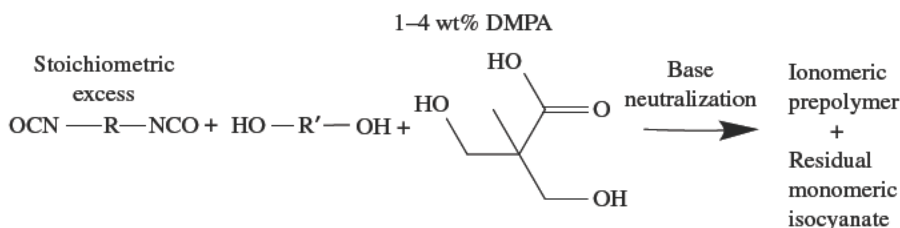


FIGURE 10.9 Synthesis of ionomeric prepolymer for PUD based on DMPA. Reprinted with permission from Ref. [30]. © John Wiley & Sons, Inc.

growth has been driven largely by regulatory initiatives to reduce VOCs in coatings and adhesives. PUDs enable delivery of a low viscosity urethane polymer to a substrate, while reducing or eliminating the use of fugitive organic solvents [29].

As the name implies, PUDs consist of particles of urethane/urea polymer dispersed in a continuous phase of water. The most common technique for dispersing PU in water involves use of self-dispersing ionomeric PU prepolymers. In this process, an ionizable moiety is reacted into a PU prepolymer structure. The most common of these moieties is dimethylolpropionic acid (DMPA) (Fig. 10.9) [31].

The polyol and isocyanate structures in PUD prepolymers can vary widely depending on final application and requirements. While PUD prepolymers are typically isocyanate terminated, they can also employ hydroxyl-terminated prepolymers for two-component waterborne urethanes.

Prior to dispersing in water, the carboxylic acid groups in the prepolymer are neutralized with a strong base such as triethylamine to convert the acid to the carboxylate. It is this hydrophilic neutralized carboxylate that serves to disperse and stabilize the particles in the aqueous phase. Immediately following this aqueous dispersion step, a chain

extender is added to the dispersion to complete conversion of the remaining isocyanate groups to the final polymer within the particles. Due to the competing reactivity of water, the selection of chain extender is limited to chain extenders with higher reactivity toward isocyanates than water. Most commonly, these chain extenders are primary or secondary polyamines that chain extend the polymer via formation of urea bonds.

The PUD ionomer process is often done with low levels of a solvent, such as acetone or *n*-methyl pyrrolidinone (NMP) to lower prepolymer viscosity in the process. In the case of acetone, the solvent is removed in a final step, while low levels of high boiling solvents such as NMP may be left in the final product.

The use of aromatic isocyanates can also be challenging in this process due to high reactivity with water during the chain extension step. Low residence time dispersion technologies for PUDs employing mechanical dispersion are reported in the literature that address reactivity challenges associated with aromatic isocyanates [32].

In the case of *nonreactive* PUDs, the polymer is fully formed prior to application, and properties develop solely on the basis of drying and coalescence of the PU particles.

Two-component *reactive* PUDs employ two separate dispersed phases that react with each other during the drying phase. This type of technology is utilized both in coating and adhesive applications. Cross-linking of the polymer during the coating step can provide improved polymer properties versus a single-component PUD.

Apart from backbone alterations to make PUDs more water compatible, process innovation to obtain ever-smaller dispersion particles and involving ever smaller amounts of organic solvents has been evident [33, 34]. As shown in Figure 10.9, modification of the backbone with a monomer building block such as DMPA can facilitate compatibilization of the PU chain with water. However, this is usually not enough to result in a desirable adhesive product, and the process of dispersion is highly optimized by manufacturers. Many of these production methods are batch operations where all the ingredients of the dispersion are added to a single reaction vessel (in the appropriate order and amounts), heated, mixed, degassed, filtered, and so on, (and stored for packaging. Continuous operations have also been developed, which can minimize the need for storage of large amounts of inventory [35]. The ability to produce volumes at times and places near to their application is helpful extending shelf life stability for the customer. Figure 10.10 is a simplified block diagram for the batch process.

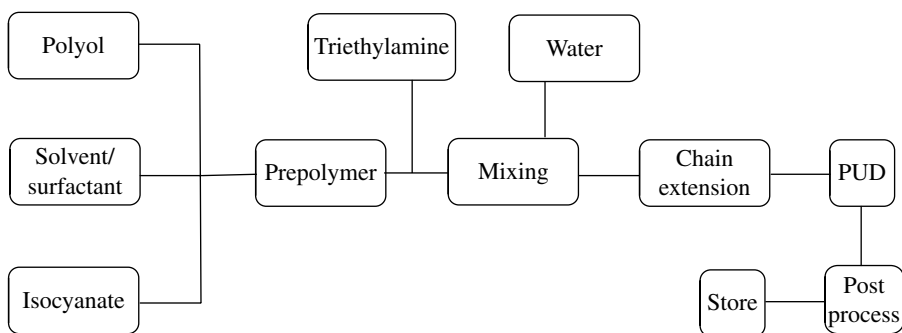


FIGURE 10.10 Batch process for PUD production.

The process in Figure 10.10 is not without complications. The polyols (including the DMPA) are added to the isocyanate that is present in excess in a prepolymer process. Solvent, surfactant, and catalyst can be added according to the component and process requirements. The acid groups of the prepolymer are neutralized and mixed rapidly with added water. While the neutralizing agent (usually triethyl amine) imparts solubility to PU in water, it also facilitates reactions of isocyanates with water and also potentially of free isocyanate–isocyanate reactions (see Chapter 3). When water is added to the neutralized prepolymer (with energetic mixing), the uncontrolled isocyanate reactions can result in increased system viscosity and complicate the dispersion of the PUD particles into small particle sizes. Diamines such as ethylene diamine, 1,2 propane diamine, or hydrazine are added to the prepolymer to complete the polymerization process by chain extension, finishing formation of the PU backbone. The role of added solvent (i.e., NMP, MEK and toluene) is to compatibilize particle-phase/continuous-phase viscosities and facilitate shear-induced particle breakup into very small particles. Optimized processes can result in the formation of submicron particle sizes. The process solvent can then be removed in a postprocessing step, or be included in the final formulation to facilitate adhesive (or coating) application attributes. PUD produced by this or similar batch process using internal ionic stabilization can also suffer from instabilities caused by unintended excursions in pH, ionic strength, or temperature.

Some of the weaknesses of the batch process can be mitigated by a continuous process as illustrated in Figure 10.11. The obvious difference between batch and continuous is the multistage mixing and the nonrequirement of solvent. In the continuous process, the prepolymer (ionic or nonionic) is formed and subsequently sheared with high energy concomitant with the addition of surfactant and a small amount of water. The process is controlled to invert an initial water-in-oil dispersion to an oil-in-water dispersion despite the small volume ($\sim 10\%$ v/v) of water. Additional water and optional diamine chain extender can be added in a subsequent mixing step to dilute the dispersion to a desired solid content (Table 10.6).

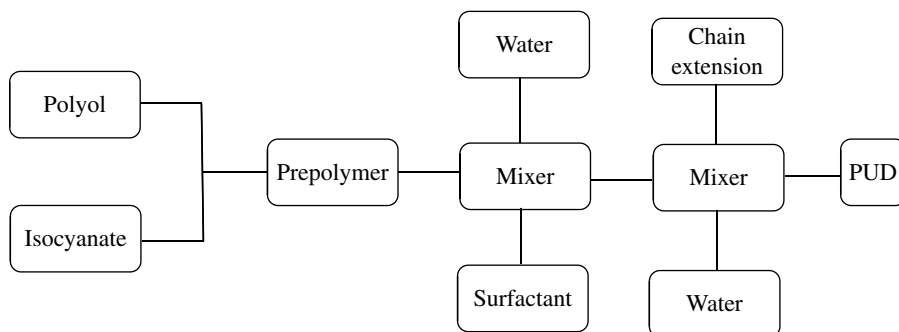


FIGURE 10.11 Block diagram for continuous process for making PUDs via a high inverted phase process.

10.2.2 Trends in PU Adhesives

While the patent literature is notably poor at providing insight into fundamental science, it is the clearest way of understanding the future of a technology and market. This is because the patent literature represents a sizable investment by a company or individual on what is believed will be desirable by customers and market competitors in the next-generation product. Further, defense of a patent asset requires that the technology on which a patent is based must be protected by patent prior to its commercial introduction. While a single patent may not be instructive as to the direction of future innovation, a clear trend in industrial patent activity can be unmistakable.

Adhesives in general, and PU adhesives in particular, are highly formulated and can bring a high degree of value to specific customers with one formulation, while a small variation will meet the needs of another customer. This circumstance and the very keen level of competition among adhesive providers lead to a very active patent landscape. Our previous category analyses by patent have focused on the activities of major feedstock providers. Major chemical producers are actively protecting their adhesive intellectual assets via patents, especially in defense of their systems house businesses. Figure 10.12 quantifies patent activity from the years 2000 through 2014, of major international integrated manufacturers of PU building blocks, as well as some of the major manufacturers of formulated adhesive systems. While the number of patents among this group is high, it useful to consider that over the time frame characterized by Figure 10.12 over 1900 patents dealt with PU adhesives as either compositions of matter, methods of manufacture, or applications. Of the over 1900 patents, about half were solely concerned with adhesive composition of matter, about 100 were associated with the process of making or applying the adhesive, and the remainder were related to the use of the adhesive.

TABLE 10.6 Composition and properties of a PUD adhesive

Component	Amount	Comment
2000 g/mol 12% EO-capped PO/EO triblock polyol	41.3	Prepolymer component
2000 g/mol PTMEG	36.1	Prepolymer component
MDI	18	Prepolymer component
1000 g/mol methoxy ethylene glycol	2	Surfactant
1000 g/mol polyethylene glycol	2	Surfactant
Sodium dodecyl benzene sulfonate	3	Surfactant
% NCO (in prepolymer)		2.5%
Molecular weight prepolymer (g/mol)	3350	
1,2-propane diamine	2.45	Chain extender
Molecular weight PU polymer (M_w)	88 K	Polydispersity $M_w/M_n = 4.8$
% solids	39%	
Viscosity	29 cps	
Particle size	230 nm	
Adhesion nylon to PET	>4 lb/in	Cohesive substrate failure
Adhesion polyethylene to Al foil	2.4 lb/in	Adhesive failure

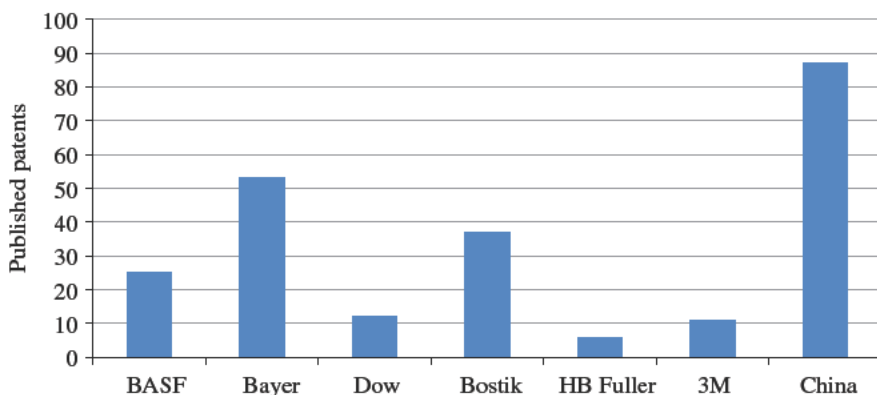


FIGURE 10.12 Patent activities from years 2000 to 2014 of major international polyurethane building block manufacturers and major manufacturers of formulated adhesives. Comparison is made to all patents on the same subject filed in the Chinese language.

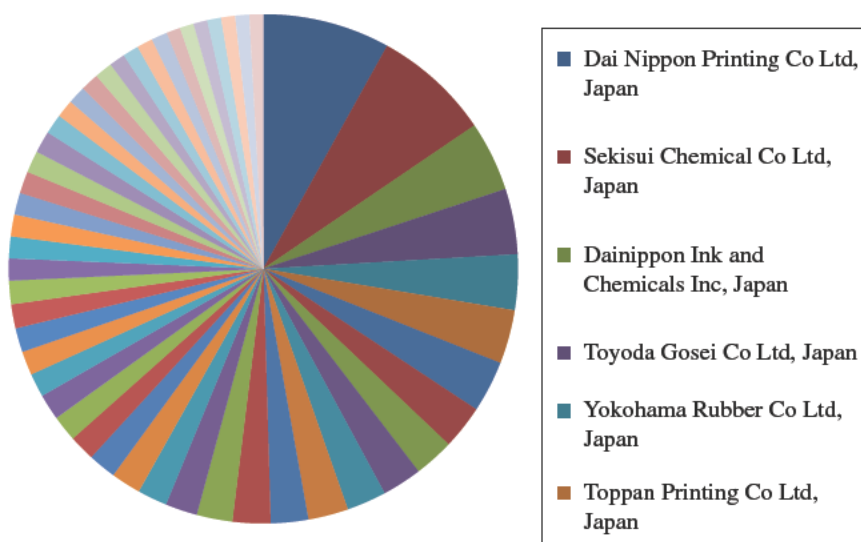


FIGURE 10.13 Global patent activity for polyurethane adhesives for companies having more than 5 patents. The top five patenting companies (by number of publications are indicated). The graph shows the large number of formulators and manufacturers active in the competitive marketplace. (See insert for color representation of the figure.)

For additional perspective, a broader view of patent activity is provided in Figure 10.13 illustrating the distribution of patent activity of all companies with more than five patent publications over the 2000–2014 time frame. Figure 10.13 shows that the top five patenting companies are Japanese concerns. While representative of activity, this figure does not filter out kokai patent publications that are unexamined applications. A kokai is often promulgated by a company for the purpose of destroying intellectual novelty

rather than a sincere attempt to protect an economic asset. In any case, it is also notable that nonchemical companies appear to participate so heavily in the landscape. This can be misleading; many venerable and very sizeable Japanese concerns do not change their historical names to reflect the highly diversified portfolio of products they provide and, just as importantly in the adhesives field, utilize in their business.

As mentioned earlier, about half of PU adhesive patent activity is concentrated on new formulations and compositions for achieving new performance criteria. A partial review of composition of matter patents shows that the majority of new formulations are in fact novel arrangements of conventional materials (Fig. 10.14). No doubt the resulting performance is the basis for asset protection. A similarly abridged analysis shows a varied list of well-known PU adhesive applications (Fig. 10.15). Any trend analysis would probably focus on the relatively large number of application patents

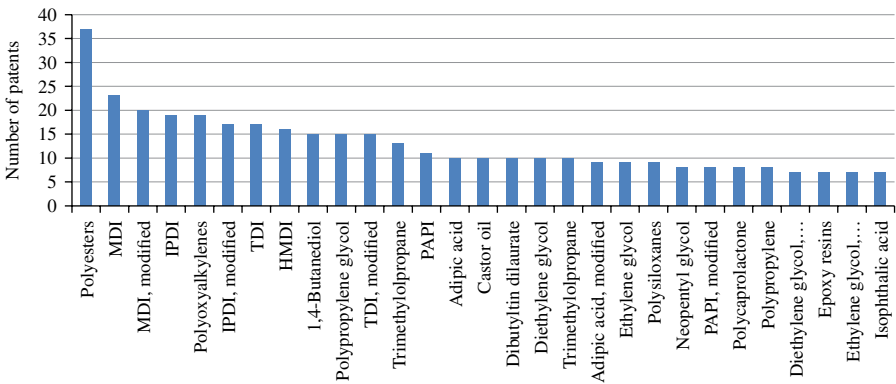


FIGURE 10.14 Adhesive patent activity subject based on protecting specific polyurethane compositions of matter. Result indicates that innovation is based on new formulations of well-established materials. Years 2000–2014.

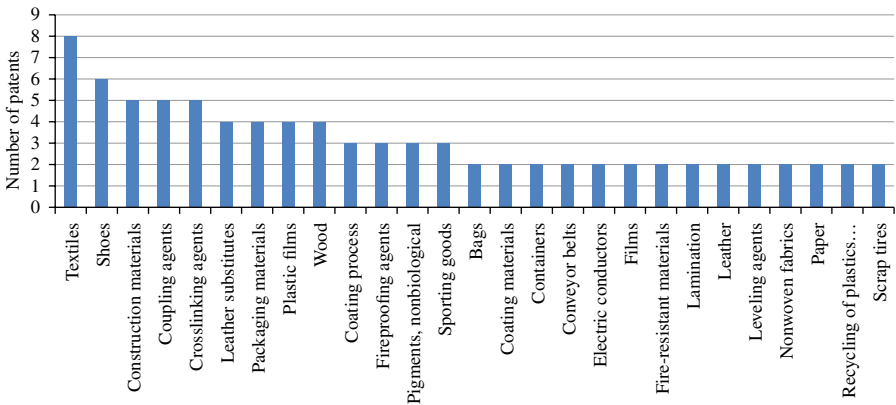


FIGURE 10.15 Analysis of PU adhesive applications patent activity for the years 2000 through 2014. Applications do not suggest any discontinuity with well-established applications.

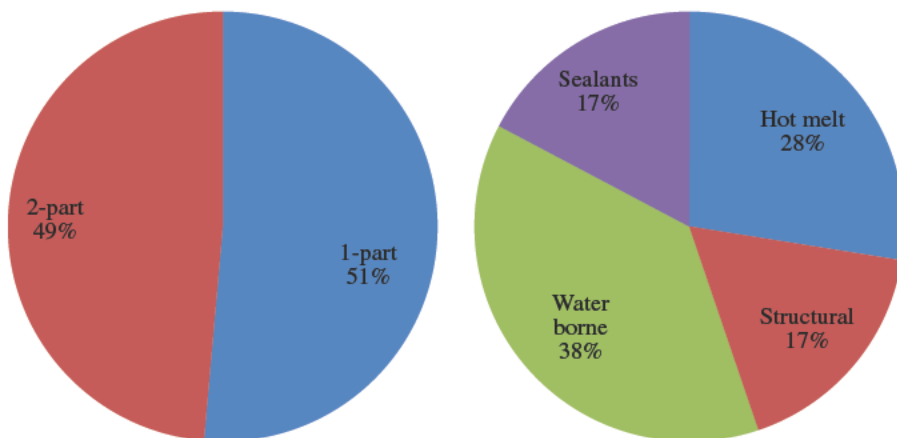


FIGURE 10.16 Distribution of patents based on their delivery format and general application category. Data reveal the global movement toward low VOC formulations.

focused on adhering articles of clothing. In fact, a general conclusion of the future trends might point to dissemination of conventional materials into conventional applications to achieve higher performance.

Patent activity since 2000 has been evenly distributed between two-part and one-part formats suggesting that innovation is being driven equally between performance and convenience (Fig 10.16). Further, patent activity across adhesive technology platforms suggests that while waterborne and hotmelt platforms are the most active fields of innovation, there is substantial work across the spectrum and no particular platform is out of favor.

Last, it is useful to consider that while PU represent about 6% of all plastic manufactured, it represents slightly less than 3% of all adhesives patents during the time frame 2000–2014, suggesting that lower cost or specific applications, such as electronics and structural adhesives, may represent areas of more intense current activity. The highest growth in patent activity is in the fields of reactive PU hotmelts and in waterborne PU adhesives.

10.3 COATINGS

Coatings is an important and rapidly growing value-added application of PU chemistry [36, 37]. All the material aspects that make PU into successful elastomers, adhesives, and thermoplastics translate to making high-performance coatings as well. Thus, PU coatings are valued particularly for durability, abrasion resistance, aesthetics, and formulation flexibility. In addition, like PU adhesives, PU coatings can be delivered in numerous formats to meet the process requirements of almost any coating operation.

Quantifying market consumption based on type and application is complicated by the varying classification of a coating. For example, should urethane modification of

an acrylic or epoxy coating be counted as urethane? Should a sprayed truck bed liner be grouped with a sprayed clear furniture coating? Is the common means of application a sufficient qualification to group these very different products within the same category? Some analyses of usage do, and others do not. Variance in market data reflect simply an individual perception of what a coating is. Another quantitative variable is counting volumes of formulated (and diluted) coatings versus just the volume of PU in that coating.

Another distinction of coating classifications are those that are defined as “architectural” and those defined as “industrial” [38]. Industrial coatings are all of those coatings applied at a manufacturing facility. Architectural coatings are those meant to be applied in or onto buildings. There is obviously overlap in the coatings themselves since wood coatings can be used in both places as can paints and alkyd coatings. The distinction is merely the location, and in some cases formulation specification, consistent with use by unlicensed individuals in unventilated environments. Thus, it is reasonable to approach coatings market data with the perspective of viewing a snapshot that may reflect a set of definitional biases along with the usual lack of precision accounting for volumes consumed by many thousands of manufacturers and billions of consumers.

While absolute volumes are potentially imprecise, the ratio of volumes has been relatively constant and can perhaps represent useful data for comparison. Figure 10.17 shows the proportional amounts of polyols and isocyanates used in coatings. For specialty performance products such as coatings, the choice of building block is anything but arbitrary. The use of specific polyols and isocyanates are designed to meet stringent requirements for the application; and while price is a consideration in every real function, performance will often be the driver of what particular PU

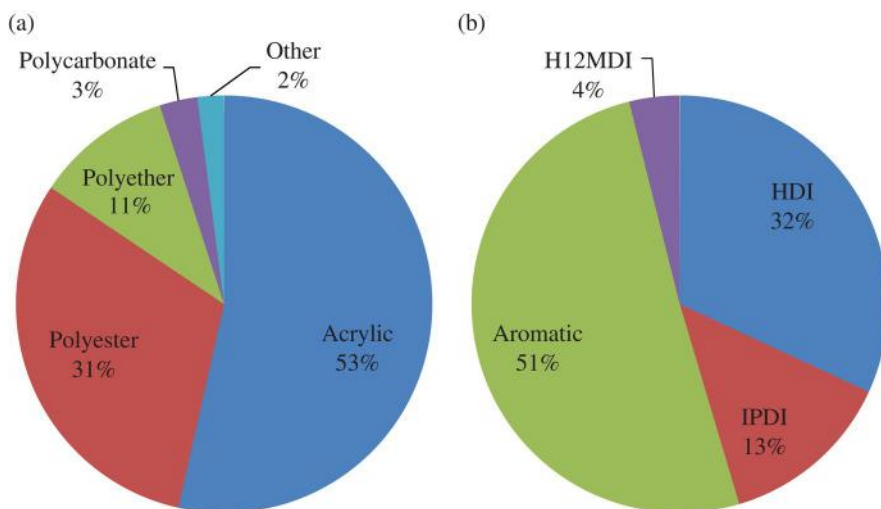


FIGURE 10.17 (a) Distribution of polyol consumption in polyurethane coatings based on chemistry and (b) distribution of isocyanate consumption in polyurethane coatings based on chemistry.

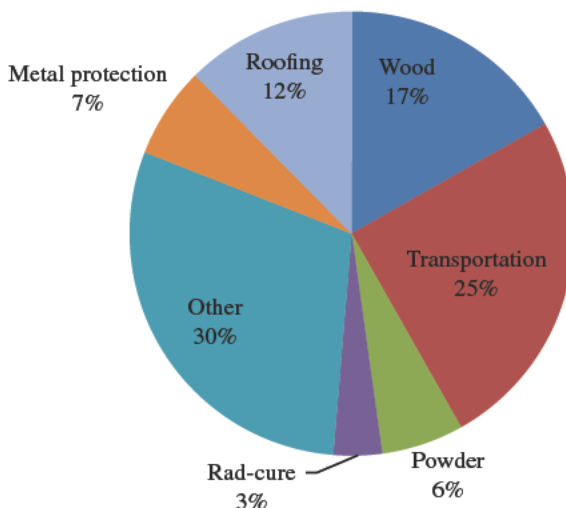


FIGURE 10.18 Distribution of industrial applications employing polyurethane coatings. The importance of “other” is consistent with the high service requirements for participation in this market, providing custom solutions for smaller, customer-specific applications.

chemistry and product format will be used [39]. In this regard, the applications that use PU-based coatings and their approximate ratio is shown in Figure 10.18. Architectural coatings use little PU resin and represents about 10% of total PU resin used for coatings and is not included in the figure. Most of this PU is in the form of PU-modified alkyd coatings for wood coverage. Additional architectural volume is PU waterborne dispersions for wood coatings.

Table 10.7 is a list of PU coating technologies as defined by ASTM conventions including a list of applications for which those technologies are found useful. The technology choice (i.e., solvent-borne versus waterborne) reflects the demands and the conditions of application.

As a rule, almost all coatings that are applied to impart an aesthetic appeal utilize aliphatic isocyanates since their tendency to yellow is much reduced relative to aromatic polyisocyanates (see Chapter 2). However, aromatic polyisocyanates are used for coatings that are nondecorative, are part of an interior lining, have an underground function, or are part of a formulation that does not use a solvent.

Much as any technology, coatings are tested for their performance attributes. Given the range of environments and functions for coatings, the number of standard tests is quite large. Table 10.8 is an abridged list of tests commonly applied for coatings testing. The Standard Guide tests should be consulted initially to provide a complete list of standards that apply to numerous applications for the specified technology. Since testing of coatings is largely a pursuit of industry, many individual tests are automated or have commercially available equipment that are designed and sold for specifically testing for an ASTM standard, and provide a modicum of standardization across different laboratories. Regardless, it is not uncommon for separate labs

TABLE 10.7 ASTM classification of polyurethane coating based on format and method of cure and their predominant application areas

ASTM convention	Description of technology	Applications
Type I	One-part nonreactive, unsaturated aliphatic esters; no free isocyanate groups in coating, cure by oxidative cross-linking of unsaturated groups and solvent evaporation. Uses soybean or linseed oil.	Architectural floor and maintenance, topcoats. Better performance than unmodified alkyds
Type II	One-part moisture curing, contains free isocyanates, reacts with environmental water and isocyanate reactive groups on the substrate surface. Polyether or polyester soft segments. Can use various blocking techniques to preserve isocyanate reactivity for extended shelf life.	Leather, concrete, maintenance
Type III	One-part heat cure. Uses blocked isocyanates that are liberated upon heating to react with isocyanate-reactive components in the formulation. Polyether or polyester, often phenol, caprolactam, or cresol-blocked aliphatic polyisocyanates or TDI.	Coil and electric wire
Type IV	Two-part solvent-borne. One part is the prepolymer polyisocyanate, whereas the other is the polyol(s), catalyst, and all other formulation components such as solvents, pigments, and other additives. Acrylic and polyester polyols are common components. Also can use hydroxyl functional alkyds. Ambient or heat cure. Pot life can be an issue and can be influenced by using aprotic complexing solvents.	Plastics, wood furniture, marine exteriors
Type V	Two-part high solid (>50%) coatings. One part is a prepolymer and the other is polyol, usually acrylic, polyesters, or polyethers. Considered high-performance coatings can have limited pot life complicating application.	Leather, wood, automotive clear coats, refinishes, aircraft, bus, truck, industrial structure maintenance coatings
Type VI	One-part nonreactive low solid (<20%) solvent borne. Referred to as a lacquer. High gloss film forms upon solvent evaporation	Textiles
Powder coatings	One-part reactive system using caprolactam or 1,2,4 triazole blocked aliphatic isocyanates especially IPDI and H ₁₂ MDI, polyester, and epoxy-modified soft segments. Viscosity must be controlled and kept low to ensure powder coalescence during application and bake.	Automotive exterior panels and parts, wire, electrical transmission equipment (i.e., transformers) reflective surfaces, metal surfaces, outdoor lawn furniture.

TABLE 10.7 (Continued)

ASTM convention	Description of technology	Applications
Radiation	High solid coatings, rapid cure, high gloss, not practical for home use or complex shapes. Made by reacting isocyanate-capped prepolymer with hydroxyl functionalized acrylate or methacrylate. Requires use of photoinitiators in formulation. Any isocyanate can function but usually aliphatic.	Manufactured wood flooring, cabinets, metal surfaces, plastic.
Waterborne	Broadly applied to one- and two-part systems using aliphatic or aromatic isocyanates. Reduces VOC exposure, high growth of application in all geographies, can be used in hybrid technologies like uralkyds and PU acrylates. May be formulated with water-soluble organic solvents for better solubilization of components. May also use defoamer. Cure speed/drying is less of an issue as percentage of solids have increased.	Wood coatings, decorative coatings, artificial leathers, textiles, plastics, inks, architectural, automotive

Powder, radiation cure, and waterborne coatings do not yet fit into the ASTM conventions but are included here as well.

TABLE 10.8 Abridged list of standardized tests and methods for characterizing coatings

Test	Standard description
D5324	Standard Guide for Testing Water-Borne Architectural Coatings includes list of tests for flat interior and exterior latex paints, waterborne floor paints, and semi- and high gloss latex paints. References 80 standards for characterization of architectural coatings
D6577	Standard Guide for Testing Industrial Protective Coatings is specifically intended for paints applied to substrates on-site of structures and buildings, especially where subject to corrosive environments, as industrial, urban, and marine environments. References 129 standards for characterization of industrial protective coatings.
D5146	Standard Guide to Testing Solvent-Borne Architectural Coatings includes interior low-gloss wall finish, interior gloss and semi-gloss wall and trim enamels, exterior house and trim coatings, and exterior and interior floor enamels. References 75 standards for characterization of solvent-borne architectural coatings.
D3451	Standard Guide for Testing Coating Powders and Powder Coatings, particularly those applied by electrostatic, fluidized bed, or alternative method. References 85 standards for characterization of powder coatings and coating characteristics.

(Continued)

TABLE 10.8 (Continued)

Test	Standard description
D3730	Standard Guide for Testing High-Performance Interior Architectural Wall Coatings. High performance denoting coating that are tougher, more abrasion, and more stain resistant than usual coatings. References 49 standards for characterizing this class of architectural coatings.
D2832	Standard Guide for Determining Volatile and Nonvolatile Content of Paint and Related Coatings. Applicable to all ASTM coating types as well as powder coatings, and water-based coatings. References 15 other standards for specific coating types that apply in conjunction with the present standard.
D5178	Standard Test Method for Mar Resistance of Organic Coatings. Coating is applied to a flat surface and progressively challenged with a weighted stylus that is incrementally loaded until coating failure.
D3732	Standard Practice for Reporting Cure Times of Ultraviolet-Cured Coatings. Specifies UV cure but is generally applicable. Involves application of the coating to a desired substrate at a desired thickness and curing for incrementally longer exposure. Cure is measured by property measurement including impact resistance, hardness, solvent rub test, abrasion resistance, stain resistance. The shortest time that yields a cured film is the cure time.
D7394	Standard Practice for Rheological Characterization of Architectural Coatings using Three Rotational Bench Viscometers. Applicable to waterborne architectural coatings. Instructions for using a Brookfield viscometer, a paddle viscometer, and a cone-and-plate-type viscometer for sampling behavior in low-, medium- and high-shear rates.
D4708	Standard Practice for Preparation of Uniform Free Films of Organic Coatings. Useful procedure for direct determination of coating physical properties including permeability independent of substrate. Involves casting of film on to either fluorinated sheet, silicone-coated sheet, or halosilane-coated glass followed by cure and sample removal.
B499	Standard Test Method for Measurement of Coating Thicknesses by the Magnetic Method: Nonmagnetic Coatings on Magnetic Basis Metals. Nondestructive test method for measuring nonmagnetic coating thickness using commercially available device. Device monitors the magnetic flex density. Method cannot distinguish thickness of individual layers, only cumulative thickness.
D2134	Standard Test Method for Determining the Hardness of Organic
D4366	Coatings with a Sward-Type Hardness Rocker. Common method in coatings industry for determining hardness and cure. Monitors hardness and cure by time the amplitude of sinusoidal oscillation of a specific tester. Linear relationship between this technique and other techniques such as the Koenig pendulum hardness tester, also commonly used (D4366 withdrawn).
D6577	Standard Guide for Testing Industrial Protective Coatings. Includes industrial and architectural coatings with reference to 126 related standards including salt spray testing, graffiti resistance, MEK double rub, and so on.
D6943	Standard Practice for Immersion Testing of Industrial Protective Coatings Covers testing of samples at standard temperature and pressure, with a temperature gradient, and at constant temperature and increased pressure. Many applications, including can coatings.

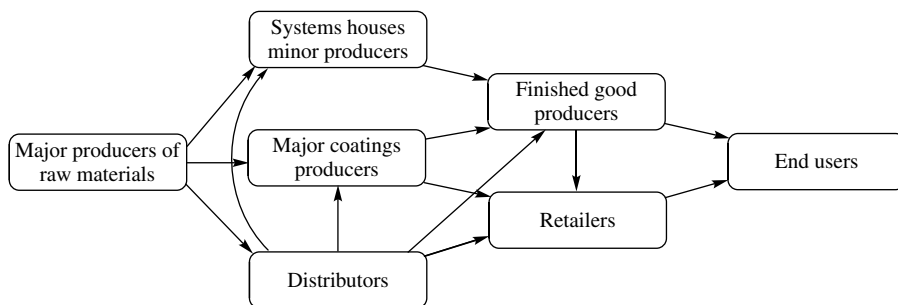


FIGURE 10.19 Simplified supply chain and commercial relationships between polyurethane coatings market participants.

to achieve different results due to differences in surface preparation and differences in coating application, which every standard warns, is critical to results [40, 41].

The PU coating industry has much in common with the PU adhesive industry making it convenient to group them together. In both cases, the application is a film that must adhere to a surface and cure within a predetermined time. The forms, solvent-borne, waterborne dispersions, moisture cured, and one part and two part, are all in common with the adhesives industry. Also in common is the general similarity in industry structure depicted in Figure 10.19. This figure (simplified as it is) depicts the inter-relationships along the supply chain in situations where participants can be simultaneously customers, suppliers, and competitors. This entangled system creates market opportunities and vulnerabilities that are very different from a landscape of limited and well-known competitors and customers [42]. For instance, the coating formulator position can be exposed to unusual pressures as they can be simultaneously squeezed by high raw material costs that can coexist with depressed consumer demand depressing final product prices. While the coatings producer can purchase from alternative suppliers to create price competition, these suppliers are relatively few in number, and their commodity feedstocks tend to have well-characterized supply, demand, and pricing. Like other products that may only have subtle differences (think gasoline), their prices tend to move quickly and in unison up and down. Price differences, such as exist, are related to producer efficiency and spot supply conditions, and tend to be relatively small. Even noncommodity raw materials such as aliphatic isocyanates are less price elastic due to limited volumes and limited producers resulting from exigencies of phosgenation (see Chapter 2) [43].

10.3.1 PU Coating Formulations

Coatings often have a decorative and a protective function. Since many coatings are exposed to the environment, especially to light, they are often formulated with aliphatic isocyanates to circumvent photolytic degradation mechanisms (see Section 2.2.3). Manufacturers of aliphatic isocyanates have modified aliphatic monomers to provide cross-linking potential for coatings by trimerizing isocyanates into isocyanurate rings. The resulting ring structures are very thermodynamically stable,

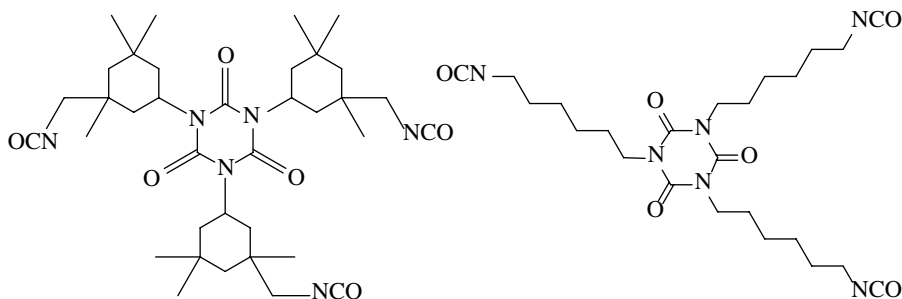


FIGURE 10.20 Structure of aliphatic isocyanate trimers (IPDI and HDI) commonly employed in decorative and protective polyurethane coatings.

have the potential to create three-dimensional networks through three-functional cross-links, improve solvent resistance, and promote formation of clear amorphous/glassy films by inhibiting phase separation of any chain extended phase. Figure 10.20 are the structures of aliphatic isocyanate trimers commonly employed for PU coatings. H_{12} MDI that is used in limited coating applications is not commercially supplied as a trimer. The use of HDI trimer or IPDI trimer is a matter of coating requirements, and it is not unusual for a coating formulator to mix them in a single coating to obtain optimized properties. The linear aliphatic HDI trimer is employed to impart flexibility, and uniform reactivity. The cycloaliphatic IPDI trimer produces enhanced coating rigidity and higher film hardness. The secondary isocyanate of IPDI is slightly less reactive than the primary isocyanates of the HDI trimer, and results in longer pot life and slower reactivity as measured by tack-free times.

10.3.1.1 Two-part Solvent-Borne Coating The two-part solvent-borne coating formulation depicted in Table 10.9 is one that might be used for an automotive top coat, refinish, or general industrial coating. It utilizes a linear acrylic polyol with a binder T_g of 48°C , OH number of 59.4 (OH equivalent weight 944), an M_n of 2941 g/mol dissolved in a xylene-*n*-butyl acetate mixture with a viscosity of 2200 cps at 40% solids. The total solids content of the formulated coating is 55% adjusted with added butyl acetate. Formulations were prepared with trimers of HDI and IPDI. Coatings were applied at room temperature and cured at 60°C for 3 h. Final coating thickness was $25 \pm 2 \mu\text{m}$ for both coatings.

The formulations of Table 10.9 are simplified to demonstrate coater binder properties separate from properties influenced by other components such as pigments or rheological and stabilization additives. The data illustrates the influence of aliphatic isocyanate on coating properties. The disparity of properties between trimers of HDI and IPDI naturally leads formulators to attempt the best of both worlds by blending [44, 45]. While blending of IPDI with HDI does moderate the coating performance between the extremes, it is often not a linear response and the properties of different coating properties do not change with the same concentration function. Thus, while change in Koenig hardness may change linearly with isocyanate composition, the mandrel test of flexibility may not change appreciably until the isocyanate

TABLE 10.9 Formulation and properties of a two-part solvent-borne polyurethane coating

Component	Formulation 1	Formulation 2
Acrylic polyol	9.1	9.1
Dibutyltin dilaurate (catalyst based on polyol weight)	100 ppm	100 ppm
HDI trimer	NCO/OH = 1	
IPDI trimer		NCO/OH = 1
Solvent <i>n</i> -butyl acetate	To 55% solids	To 55% solids
Properties		
Gel time (min)	35	140
Gel content (%)	91	70
Pencil hardness (ASTM D3633)	H	2H
Koenig hardness	107	122
Mandrel flexibility (ASTM 4338)	100%	65%
MEK double rubs	>100	15

Coating properties are affected in predictable ways by choice of isocyanate cross-linking and formulators often mix them to balance performance.

composition is very close to a concentration limit. In addition, change in the chemical resistance of the coating may follow an “S” curve suggesting some kind of required network formation to affect properties.

10.3.1.2 Waterborne Coatings As discussed in Section 10.2.1.3, there has been exponential growth in patent activity surrounding aqueous PU dispersions (PUDs). A significant amount of this protection of intellectual assets has been the application of PUDs to coatings. Environmental and occupational safety and health regulations to reduce exposure to organic solvents has driven innovation and adoption of aqueous dispersion technology [46, 47]. Today PUD coatings are accepted products for coating wood, automobiles, textile fibers, leathers, fiber glass, floor polishes, and waxes among others.

Batch and continuous methods of producing PUDs were introduced in Section 10.2.1.3. PUDs can also be made in small-scale batches for the purpose of trialing coating formulations. Such a procedure might be done on the subliter scale in a laboratory hood. An example of such a preparation follows:

A three necked flask is placed in a heating mantle and the prepolymer components: polyol, dimethylol propionic acid (DMPA), diol chain extender in the solvent dipropylene glycol dimethyl ether is weighed in. The solvent is added at 1 part to 3 parts polyol. The mixture is stirred with an overhead stirrer under a steady stream of N₂ and heated to a temperature of ca. 70 °C. An isocyanate such as H₁₂MDI, IPDI or HDI is added dropwise to the stirring mixture using an addition funnel not allowing the reaction exotherm to increase the flask temperature more than ca. 5 °C. The hard segment components (isocyanate, diol, DMPA) are added in amounts to create a desired hard segment volume—usually 40–55% of the final PUD. After allowing the urethane reactions to proceed for 3–5 h at 70 °C, triethyl amine is added in 1:1

TABLE 10.10 Illustrative properties obtained for waterborne polyurethane coating obtained by a dispersion process such as specified in the section

Test	Value
MEK double rub	140
Koenig pendulum hardness	130
Taber abrasion (mg)	11
Pencil gouge resistance (ASTM 3363)	10.5
Impact resistance (ASTM 2794) inlbs	>160
Mandrel flexibility	100%

stoichiometric ratio to DMPA and allowed to neutralize the acid for ca. 15 min. The diluted polymer is poured into a plastic bottle and allowed to cool to ca. 50 °C after which the polymer solution is diluted with water (~1 part water to 1 part polymer) and stirred at high shear rate with a mixer such as a cowels blade. The polymer is allowed to complete by addition of a diamine such as ethylene diamine or 1,2 propylene diamine and allowed to agitate for approximately 1 day. The dispersion is then filtered through an appropriate mesh filter. This dispersion is now ready for coating substrates. A rheology modifier may be added to improve coating aesthetics. The coating can be allowed to dry passively for 7 days. Properties of a PUD coating such as described are given in Table 10.10.

10.3.1.3 Waterborne Hybrids While PUDs have demonstrated strong growth as a unique technology, it has been inevitable that innovation has explored PUDs blended with other dispersible polymers or hybridized with other polymer systems [48, 49]. One of the common blended or hybridized copolymer systems has been the PU-acrylic waterborne dispersion. This category has been successful because (i) each system has properties that make up for shortcomings in the other, (ii) they have compatible chemistry that makes them easily blended or hybridized, (iii) the acrylic blend can be less expensive than the pure PUD, and (iv) they are already incumbent within the coating market so that barriers to acceptance by consumers of their combination is greatly reduced. Blends tend to exhibit better hardness and weatherability than pure PUDs and better flexibility and solvent resistance than pure acrylic dispersions.

Blending dispersions is the easiest way of making a new product, and this technique is certainly utilized industrially. The acrylate monomers making up the acrylic dispersion are usually formulated to optimize hydrogen-bonding opportunities with the PUD to enhance phase stability and coating performance. Hybridized or alloyed dispersions are produced by creating covalent bonding between the acrylate and urethane polymer chains. This has been done by reacting hydroxy functional acrylic monomers such as hydroxyl ethyl acrylate with diisocyanate and then performing the radical polymerization of the isocyanate-acrylate monomer with the other acrylate monomers for the dispersion [50]. The reactive acrylate dispersion is then reacted with the PUD prepolymer and chain extender to make the new urethane-acrylate

TABLE 10.11 Composition and coating properties of a blend of acrylic and polyurethane waterborne dispersions

70% Acrylic component	45% solids 100nm average particle size, viscosity 80 cps 1% surfactant and 0.5% <i>n</i> -dodecyl mercaptan chain transfer agent employed to molecular weight and particle size
Acrylic dispersion part A 50%	63% hydroxyethyl acrylate, 25% acrylonitrile, 8% styrene, and 4% methacrylic acid
Acrylic dispersion part B 50%	4% isobutylmetacrylate, 58% methylmethacrylate, and 2% methacrylic acid, biocide (50 ppm)
30% PUD 50% solid dispersion at 50% hard segment	47% H ₁₂ MDI, 35% PTMEG (1000 g/mol), 7% 1,12-dodecane diol, 6% dimethylolpropionic acid, and 5% 1,2-propylene diamine, antifoam
2-butoxyethanol	Coalescent agent, solvent
Properties	
T_g	45 °C
Martens Hardness (ASTM MNL-46)	50 N/mm ²
Taber abrasion	90 mg
Mandrel bend test	70 mm (out of 100)
Water resistance	Very good
50% Ethanol resistance	Very good

polymer backbone. The hybrid backbone may obtain superior phase mixing and coating properties and commercial products do exist; however, the additional associated costs associated with the new product may in some cases create a barrier to implementation. An example of an acrylic-PUD system suitable for blending along with coating properties is given in Table 10.11.

10.3.1.4 UV Cured Waterborne Dispersions for Coatings While UV-cured PU coatings are not a dominant coating technology, its use is growing for wood, metal, and plastic coatings in particular. UV-cure technology will grow within its application space as the properties of the coatings improve. The concept of these coatings is that they allow for lower coating viscosity than two-part solventless formulations, and emit less VOC than solvent-borne formulations or those having unreacted monomers within the formulation. While radical-induced polymerizations resulting from UV irradiation can be fast, the need to evaporate water from the coating can slow down manufacturing line speeds [51, 52]. However, as formulations improve and solids levels increase, the waterborne coatings become an increasingly attractive option in some venues. In addition, the dual cure nature of these coatings allows for tuned cross-link densities, and the possibility of higher final coating cross-link densities at lower initial viscosity than obtained with other coating technologies [53].

The UV-cure potential of PU s is achieved by incorporating hydroxyl functional acrylate monomers into the prepolymer synthesis. There are many acrylates to choose from, but an available monomer that maximizes the available cross-link potential is the triacrylate of penterthritol. The reactive components are controlled to optimize

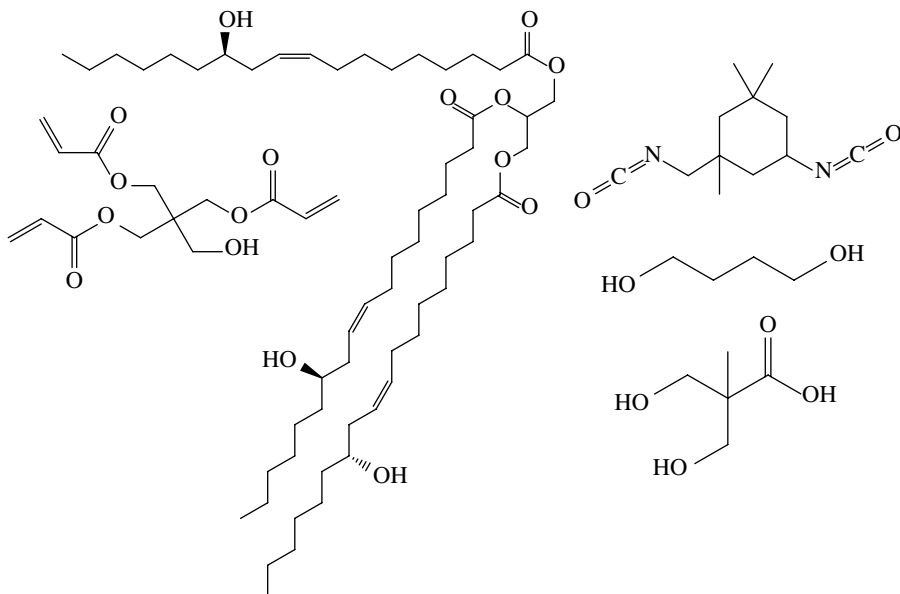


FIGURE 10.21 Illustrative composition of building blocks for making a UV curable polyurethane coating. The addition of fatty alcohol triglyceride might enhance solvent resistance.

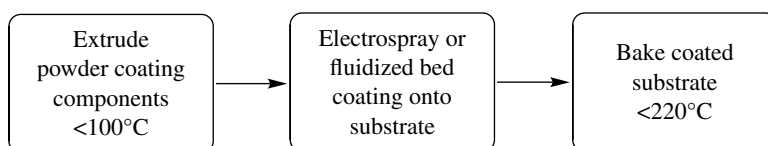
structure and performance. An example of the PU prepolymer components including the polyacrylate monomer are pictured in Figure 10.21. The composition is conventional with the possible exception of castor oil (the triglyceride of ricinoleic acid—see Chapter 2) that could potentially provide additional solvent resistance [54, 55]. The addition of the triacrylate needs to be controlled to prevent it from causing a maldistribution of molecular weights [56]. The isocyanate is added in amounts to control the final dispersion hard segment volume.

Upon completion of prepolymer formation, the prepolymer is added to cold water under high shear as described in detail previously, and the diamine chain extender (i.e., 1,2 propylene diamine or ethylene diamine) added. An appropriate photoinitiator is added last and incorporated with agitation. Depending on the photoinitiator, this may be more than 1% of the coating weight. A coated panel is then dried and subsequently passed under UV light exposure; time and energy are variables [57]. Properties of coated panels as a function of UV treatment versus no treatment are presented in Table 10.12. Coating performance data is a function of many parameters including hard segment volume, and other characteristics of the PU backbone, along with coating processing and substrate preparation.

10.3.1.5 PU Powder Coatings While PU coatings represent about 13% of the total industrial coatings market, PU powder coatings represent about 5% of the total PU volume applied to coatings. This value is consistent with powder coatings being about 5% of all coating volumes independent of chemistry. Although the overall size of the PU powder coatings application is relatively small, it is a relevant technology

TABLE 10.12 Properties of UV curable polyurethane coating tested before and after curing

Test	No UV cure	UV cured
MEK double rub	30	150
Koenig hardness	50	200
Impact resistance	>160 ft lbs	>160 ft lbs
Taber abrasion mg lost	22	7
Pencil hardness	5b	f
Pencil gouge resistance	3b	7h
Ethanol resistance 5 best 0 worst	2	5

**FIGURE 10.22** Operations of powder coating. The components of the powder coating must be blended (extruder operation), applied to the surface, and then fully integrated and cured in an oven.

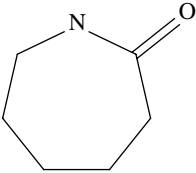
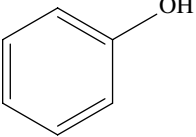
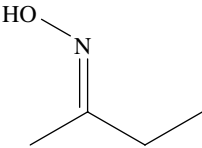
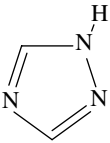
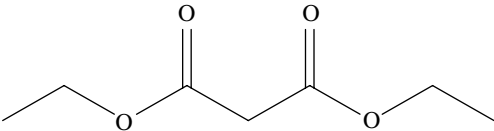
due to its lack of need for a solvent, and good coating properties. Like all PU s, PU powder coatings are valued for their durability, abrasion resistance, low-temperature flexibility, and good aesthetics. They find common use in decorative metal coatings including automotive, lawn furniture, and home appliances for instance.

The preparation of a powder coating is unlike any of the other technologies discussed earlier. The common requirement for PU and all other powder chemistries is that all of the components must be solids at room temperature [58]. They are subsequently blended into a homogeneous blend of materials in an extruder, pulverized into a powder—typically of particle size 10s of microns. The powder is then electrostatically sprayed at a substrate, or the preheated substrate is submerged into a fluidized bed of the powder. At this point, the coating is often not yet finished. The coated part is then heated in an oven at a process-dependent temperature for a proscribed amount of time. During this oven heating, the particles will melt and coalesce into a fully integrated coating. It is usually during this heating step that PU powder coatings will fully react to form a thermoset coating (Fig. 10.22).

To prevent the PU reaction going to completion at any preliminary step such as extrusion, pulverization, or initial coating, the reactants must not be available to react. This reservation is achieved by protecting (or “blocking”) isocyanate groups from reacting until they are made available at the oven temperature. Continued innovation of PU powder coatings is generally driven to optimize the coating, minimize VOCs, and minimize the temperature at which the isocyanate deblocks, and therefore reduce energy cost by reducing oven temperatures.

There are two primary methods of blocking isocyanates: (1) complexation of the isocyanate groups with a reversible leaving group (see Chapter 2) and (2) internal blocking of the isocyanate linkage by reversible isocyanate dimer formation to the uretidione (see Chapter 3). Most formulators currently employ leaving group blocking technology since it is less complex and deblocking temperature can in principle be controlled by the choice of deblocking agent. The blocking agent method suffers from the unavoidable loss of the blocking agent as a VOC in the oven cure step. To prevent unmitigated volatilization, it is often required that the volatilized blocking agent be trapped as it evolves. Several isocyanate blocking agents have developed utility for powder coatings (Table 10.13). The temperature of deblocking can be influenced by the use of catalysts, which is an area of innovation and patent activity [59–61]. While caprolactam is one of the most cited blocking agents for making PU

TABLE 10.13 Structures of chemical blocking agents and their deblocking temperatures

Blocking agent	Structure	Deblocking temperature (°C)
ϵ -caprolactam		170–190
Phenol		160–180
Methyl ketone oxime		145–165
1,2,4-Triazole		120–155
Diethyl malonate		100–110

The use of a catalyst is required to achieve the lower end of the range.

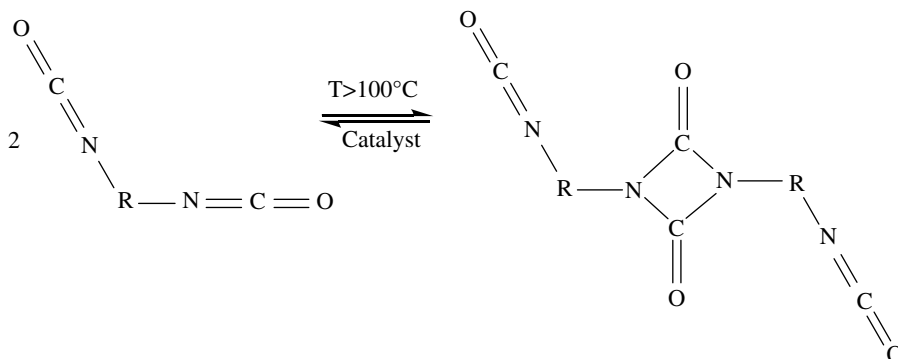


FIGURE 10.23 Dimerization of a polyisocyanate to a blocked uretidione structure. Reversion back to monomers begins at about 100°C, but it is not fast enough for industrial implementation until higher temperatures. Catalysts can lower the temperature of deblocking.

powder coatings, it has been reported that color formation is a common unintended consequence of this adduct, and other agents have become much more commonly encountered. Blocked isocyanate trimers are also available to increase cross-linking of the coating. Numerous metal catalysts have proven effective in lowering deblocking temperatures and the lower end of the temperature ranges in Table 10.13 represent catalyzed values. Patented organometallic catalysts have included dibutyltin dilaurate, bismuth tris(2-ethylhexanoate), cobalt bis(2-ethylhexanoate), zirconium bis(2-ethylhexanoate), zinc bis(2-ethylhexanoate), chromium tris(2-ethylhexanoate), and titanium tetra(ethyl AcAc), for instance.

A second method of blocking isocyanate reactions has been by reacting polyisocyanates to form uretidiones (Fig. 10.23). This chemistry is achieved efficiently using nitrogen- or phosphorous-based catalysts.

While reaction to uretidione occupies two of the isocyanates, there are obviously two isocyanates still available to react and that require blocking. It is possible to oligomerize the blocking agent making a chain of uretidione structures, and these do form in uretidione formation. More commonly, the unblocked isocyanate groups left from uretidione formation are reacted with the soft segment component of the powder coating [62, 63]. The soft segment is usually either a polyester or polyacrylic polyol—the choice of which depending on the requirements of the final product. A polyester-based PU powder coating formulation as might be encountered is detailed in Table 10.14.

A typical preparation of this simplified powder coating (Fig. 10.22) involves physical dispersion of the solid materials followed by extrusion on a low-shear extruder (~150 rpm) with mixing zone temperature at about 90°C and an exit temperature of about 110°C. The extrudate is chipped and then finely ground (average particle size 10s of microns) with subsequent sieving to remove larger powder sizes. The resulting powder is then electrostatically sprayed on a prepared steel substrate to a film thickness of 0.002 in and baked at 180°C for 10 min. Properties for this coating are given in Table 10.15.

TABLE 10.14 Formulation of an illustrative polyurethane powder coating

Component	Amount (pphp)	Amount (wt%)
Polyester component		26.5
Isophthalic acid	54	
Pentaerythritol	23	
Neopentyl glycol	23	
Catalyst	100ppm	
Acid number	7	
OH	290	
Viscosity at 175 °C cps	150	
T_g °C	63	
Isocyanate component		40
ε-caprolactam blocked IPDI		
NCO content (%) / free	15 / <1%	
NCO grm / equivalence	275	
T_g °C	50 broad	
T_m °C	70 broad	
TiO ₂		33
Flow agent		0.5

TABLE 10.15 Properties of the polyurethane powder coating of Table 10.14

Property	Value
Gel time (at 180 °C) (s)	134
Direct impact in-lb (ASTM D2794)	12
Reverse impact in-lb	8
MEK double rubs	100
Cross-hatch adhesion (% adhering)	99
ASTM D3359	
Pencil hardness	2H
Gloss 60° (%) (ASTM 5767)	85
Gloss 20° (%)	67
Color b	-1.0

10.3.2 Trends in PU Coatings

Quantifying trends in PU coatings is complex for the same reasons as the same task for adhesives. The number of patenting companies is very large, and the subject matter tends to be company specific. While many multinational PU producers have coatings businesses, they do not all have developed patent strategies relative to coatings. This is certainly a reflection of the centrality of aliphatic isocyanates to coatings technologies. Figure 10.24 is an illustrative graph of large companies and their PU coatings activity from the years 2000 to 2014 during which over 800 patents were filed worldwide specifically on protecting PU coatings assets.

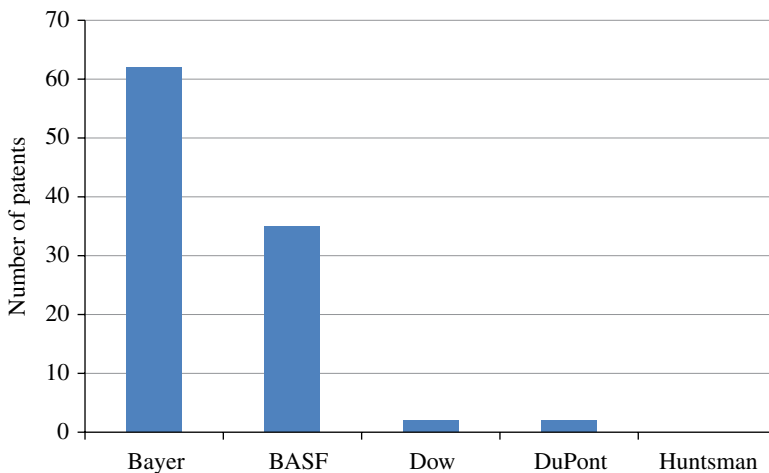


FIGURE 10.24 Patent activity for the years 2000 through 2014 by large multinational polyurethane manufacturers and DuPont de Nemours, a large multinational producer of coatings for these years. Patents are on compositions of matter, process, or applications of polyurethane coatings.

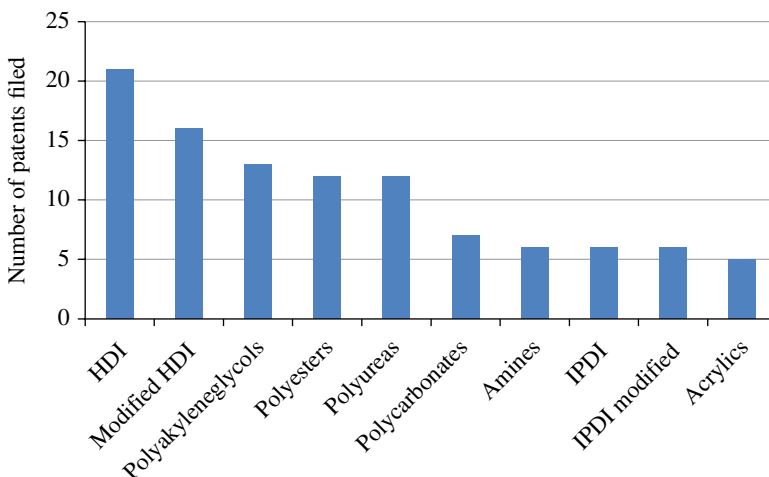


FIGURE 10.25 Bayer activity 2000 through 2014 on polyurethane coatings compositions of matter.

Bayer is by far the most active single filer of patents on PU coatings. This is a reflection of Bayer's wide portfolio of aliphatic isocyanates including HDI, IPDI, H₁₂MDI, and blocked modifications and trimers of these materials. In fact, a look at the subject matter of coating compositions (Fig. 10.25) shows that Bayer is highly focused on patenting applications and formulations associated with their product portfolio.

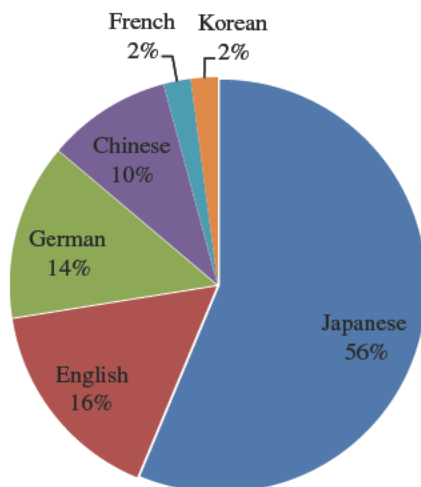


FIGURE 10.26 Patent activity for the years 2000 through 2014 by filing language as a proxy for regional application of polyurethane coatings. This analysis does not filter out filed Japanese kokai patent applications, many of which are never examined.

BASF is also a producer of aliphatic isocyanates but produces much smaller volumes than Bayer. However, BASF has widespread systems house operations. Thus, BASF protects primarily novel formulations as well as innovations pertaining to their building block manufacture. By contrast, Dow and Huntsman do not manufacture aliphatic isocyanates and their patent activity is concomitantly less (Fig. 10.24).

An alternative means of exploring technology trends is to view patent activity on a regional basis. Figure 10.26 shows the intensity of PU coating patent activity based on filing language. Japanese patent activity is by far the most prevalent reflecting their manufacturing concentrations and preferences. However, it is important to appreciate that the data in Figure 10.26 do not filter out kokai patent applications that may or may not ever be examined and are sometimes produced by manufacturers for the sole purpose of destroying patentability.

A simplified segmentation of Japanese patent activity is presented in Figure 10.27. The breadth of applications for which PU coatings are specifically the subject of patent protection is widely distributed and reflects the preferences of Japanese manufacturers for the properties PU coatings provide. A similar analysis of English and German activity shows the concentration of activity around textiles and metal coatings, particularly for automotive applications. The breadth of patent activity in all analyses does not point directly to specific trends for PU coatings apart from those relating to coating durability and aesthetic while providing improved environmental, health, and safety profiles for their use. This is amplified by the exponential growth in patent activity for production of aqueous PU dispersions for adhesives and coatings since 1980 (Fig. 10.8).

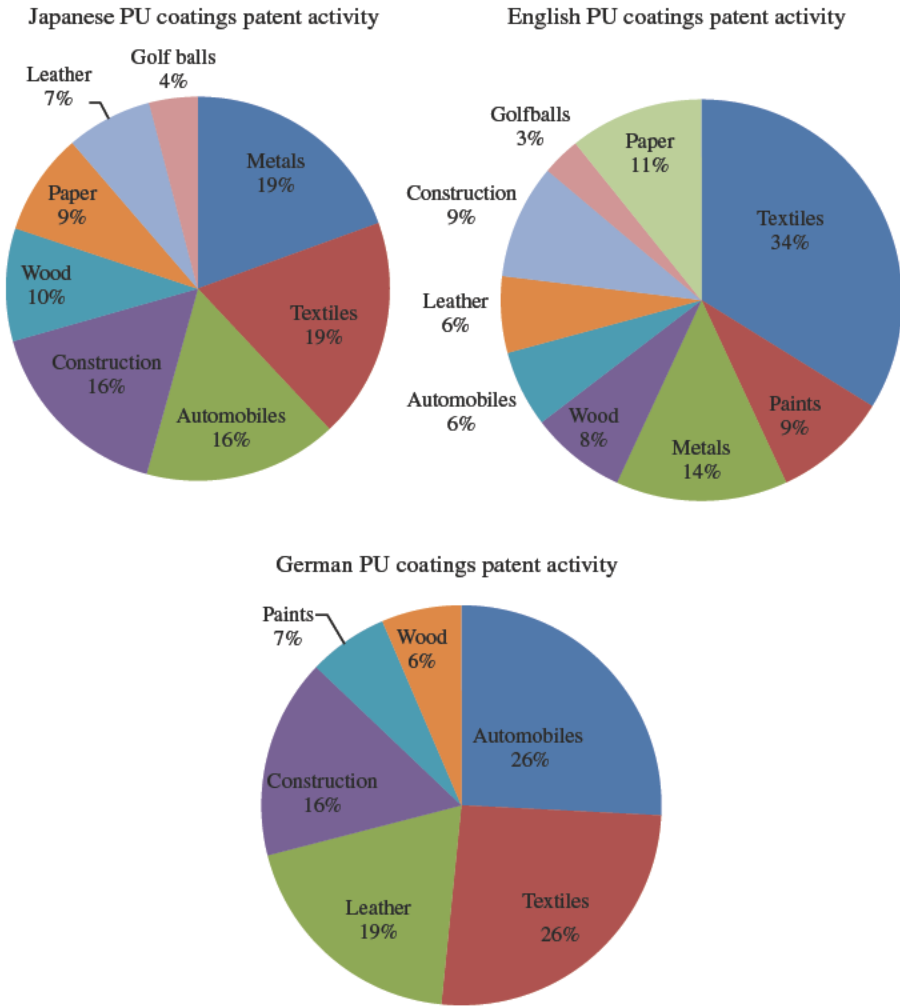


FIGURE 10.27 Distribution of filed patent documents on polyurethane coatings by application for regions of highest patent activity. Regional intensity is in automotive, textile, and construction applications.

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SPECIAL TOPICS: MEDICAL USES OF POLYURETHANE

The medical uses of polyurethanes (PU) are in many ways similar to more prosaic applications of foams, elastomers, coatings, and adhesives and in certain ways very distinctive. Virtually, every patent or academic publication on a medical application states that the material attributes of PU as a class make them ideal for medical use. Among the required PU properties valued for these applications are fatigue resistance, abrasion resistance, ability to design for biodegradability or chemical resistance, biocompatibility, wettability by bodily fluids, and ability to be fabricated into useful shapes [1, 2]. However, medical uses of PU are also substantially more complex than other uses due to the numerous ways an organism has of rejecting a foreign body and the extreme wear potential in many uses. PU can be susceptible to the numerous ways immune systems attack such as by hydrolysis, oxidation, and various enzymatically driven chain scission processes [3]. In addition, an immune system may simply colonize and coat a foreign object creating a source of thrombus (blood clots), sclerosis due to calcification, infection due to opportunistic growth, and occlusion of annular prostheses [4–6]. The criticality of performance creates a market for specialty monomers that would otherwise be too small volume and, by extension, too expensive to be commercially viable.

11.1 MARKETS AND PARTICIPANTS

The size of the medical PU market is very small by the standards of the PU industry. Accurate segmentation is difficult due to myriad small and specialty uses, but the analysis of available estimates is that 2012 global volumes were approximately 35

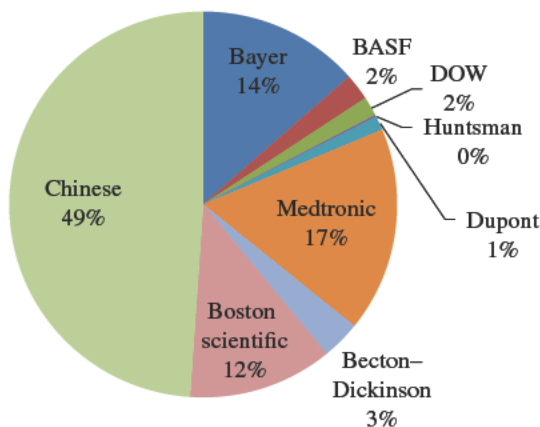


FIGURE 11.1 Patent activity from 1990 to 2014 of various industrial polyurethane producers and producers of biomedical products. Except for Bayer, which has a large life sciences businesses, PU manufacturers do not participate meaningfully in this market. 2700 total patents filed worldwide and 680 filed patents by participants in Figure 11.1.

million pounds of PU building blocks sold for medical applications. However, not including items such as mattress covers, protective gloves, and condoms, the high-performance medical market is closer to 10 million pounds with a compound annual growth rate of approximately 5% [7–9]. Volumes are split between North America, Europe, and Asia [10]. It is reasonable to expect that medical PU will find increasing use in the Asia-Pacific region [11].

Because of stringent performance and regulatory requirements for medical applications and attendant risks for performance failures, the value of PU in the medical segment is approximately 100 million dollars [12]. The majority of applications for which urethanes find medical use are associated with the requirements of an aging population (i.e., pacemakers, catheters, valves, etc.) [13]. Furthermore, the amount of innovation required to meet medical requirements, and developed in anticipation of future requirements, is astonishing. An analysis of corporate activity shows that with the exception of Bayer (which has a very sizable life sciences business), the large multinational PU manufacturers of PU components are not participating in the medical market. Instead, innovation is primarily an activity of medical device makers and, to a limited extent, universities and national laboratories (Fig. 11.1). Almost all of this activity has occurred since 1990.

The flexibility to make nearly any functional material with PU chemistry is represented by the breadth of applications that have been patented. Segmentation of PU applications according to function is shown in Figure 11.2. It shows patent activity in virtually every medical device application. The intensity of coating innovation for medical devices in many cases reflects innovation for coating a thermoplastic polyurethane (TPU) rather than a specific PU coating [14, 15].

The activity of individual companies reflects the need for corporate competitive advantage and defense against other market participants. The similarities and distinctions

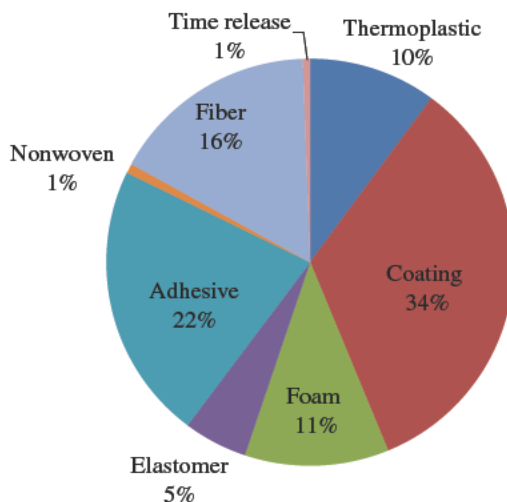


FIGURE 11.2 Distribution of patents from 1990 to 2014 filed on biomedical uses of polyurethane by technology. 2700 patents represented in the distribution.

between companies actively innovating are interesting and instructive. For instance, Medtronic is a manufacturer of numerous implantable technologies such as heart pacemakers, stents, catheters, and other surgically important products. Figure 11.3 documents the proportional areas of Medtronic Inc. PU-related patent activity by technology segment for the years 1990–2014 and the numerical activity by year. Figure 11.4 is a similar analysis for activity by Bayer AG. As mentioned previously, much of the coating innovation is related to non-PU coatings applied to a PU surgical product for a specific function. The same is true for adhesive activity. Many of the patents represent innovations improving adhesion of PU to another specific substrate or to specific biological cells [16, 17]. An interesting phenomenon in the analysis is the increasing interest in medical PU intellectual assets until the years 2009–2010 after which there was a pronounced decrease in activity. The causes for this may originate in economic or public policy concerns but are not mirrored in patent activity filed in the Chinese language on medical PU (Fig. 11.5).

11.2 TECHNOLOGY

11.2.1 Catheters

Approximately 3 million pounds of PU are consumed per year in the making of catheters [18, 19]. A catheter is a hollow tube inserted into the body for any number of procedures. They include removal of fluids such as urine or draining of fluids resulting from infection such as those that would be encountered from an internal abscess. Additionally, they are used for remote positioning of cardiac stents or balloon angioplasty. In addition, they can be critical components of other cardiac

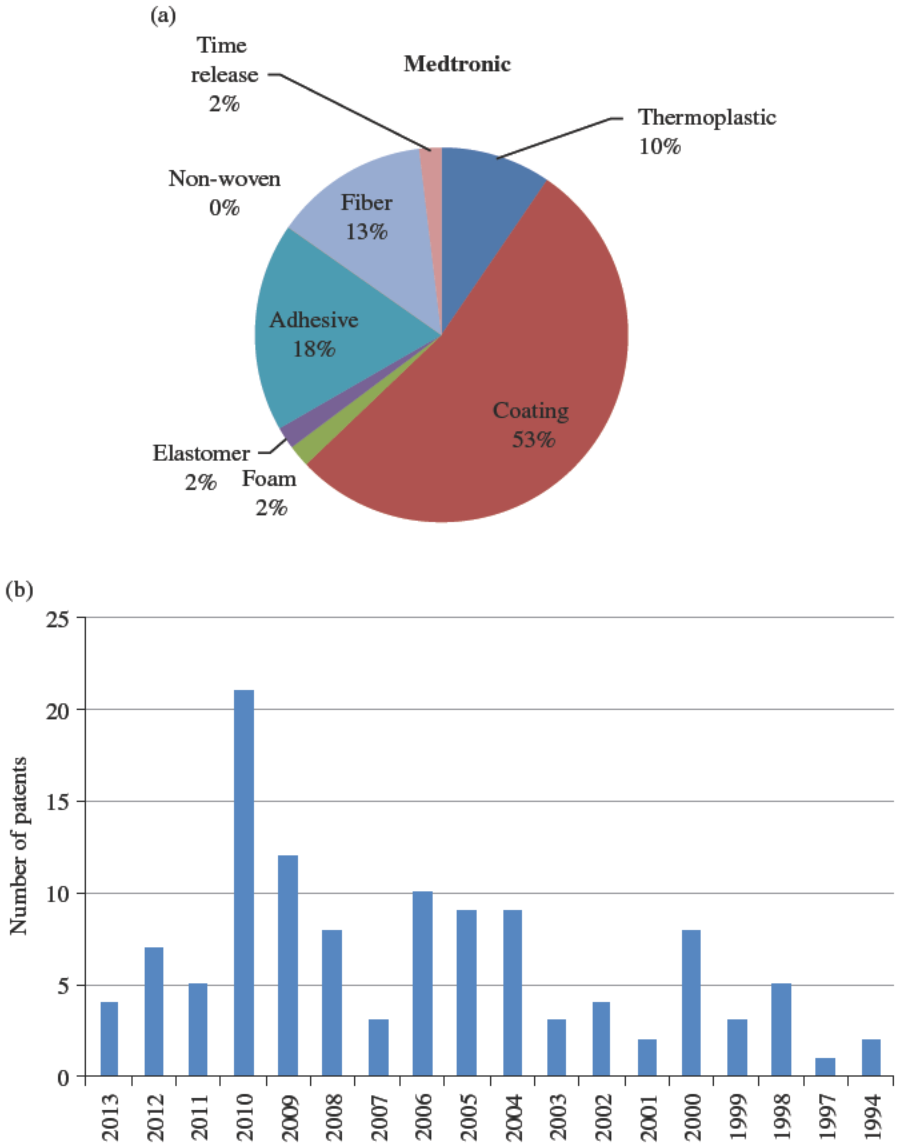


FIGURE 11.3 Patent activity for Medtronic Corporation for the years 2000–2014: (a) by technology segment and (b) by year. 59 patents filed during this time.

procedures including ablative procedures and electrophysiology testing. Many materials have been employed for catheter construction including polyvinyl chloride, polyethylene, silicones, perfluorinated polyethylene, and nylons. PU are among the preferred materials due to their flexibility, ability to engineer to the correct stiffness without kinking in use, ease of processing to appropriate form, low

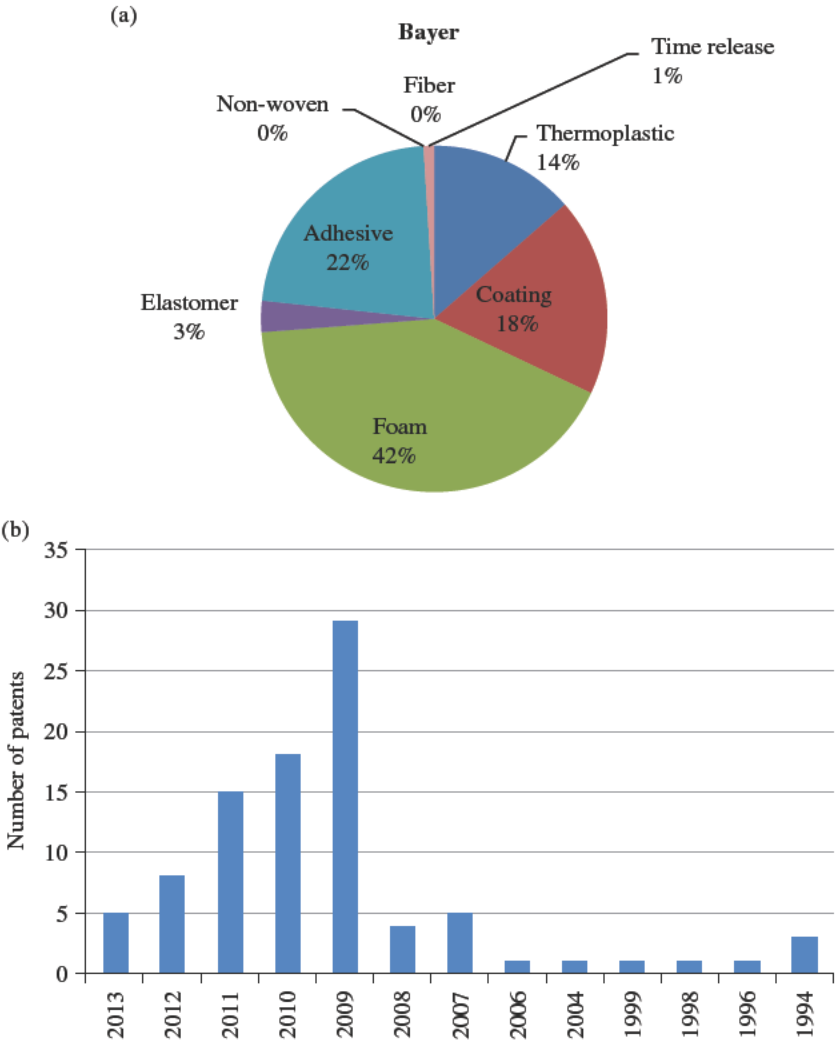


FIGURE 11.4 Patent activity for Bayer AG for the years 2000–2014: (a) by technology segment and (b) by year. 92 patents filed during this time.

coefficient of friction when wet with water, and relatively low susceptibility to bacterial colonization. The reduced susceptibility to bacterial complication is particularly important since infection is one of the most prevalent complications associated with cardiovascular procedures [20, 21]. It has been cited that between 30 and 40% of infusion therapy-related infections are complications associated with catheters beginning as local infections and potentially progressing to systemic. In this regard, it has also been reported that PU has one of the lowest susceptibilities to staphylococcus infection, possibly due to low surface adhesion energies [22, 23].

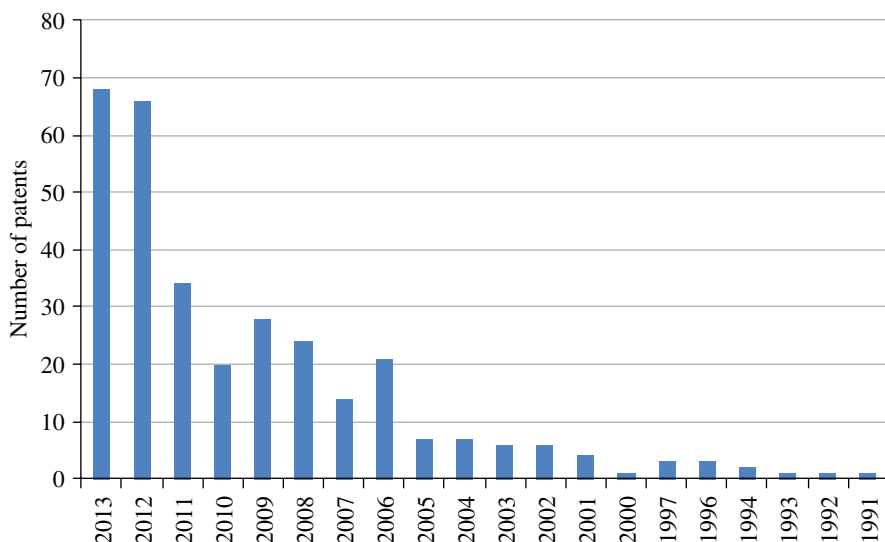


FIGURE 11.5 Number of patents filed in the Chinese language from 1990 to 2013. Total number=317.

Coatings for catheter tips with biocides for the purpose of reducing the risk of infection are a common area of patent activity [24, 25].

With the significant demands placed on a material for catheter application, it is perhaps surprising that TPUs utilized for catheters are relatively mundane. It is common for patents to specify the brand name and grade without mention of composition. In fact, it is common in medical literature and patents for the authors to simply cite “a urethane” or “PU” catheter available from a specific manufacturer. Typical medical grades of TPU are simple, and examples of their formulation are given in Table 11.1. The preference of polyether polyols over polyester polyols for catheter applications is associated with their superior low-temperature flexibility and their superior resistance to hydrolysis [26]. The simplicity of polymer design creates robustness and reliability and performance. It also makes for a predictable and reproducible substrate for subsequent surface treatments improving specific catheter functions and antibiotic performance [27].

11.2.2 Wound Dressings

Approximately 5 million pounds of PU per year are consumed making wound dressings [28, 29]. The role of a wound dressing is to provide protection to damaged skin following an operation, a burn, or a laceration, for instance. The dressing can be occlusive such that the wound is completely isolated or can be nonocclusive such that there is a semipermeable membrane or foam capable of absorbing fluids produced by the wound and transmitting gases. Wound dressings can also come with various surface treatments to prevent infection, to prevent adhesion, or to promote more rapid

TABLE 11.1 Formulation and properties of thermoplastic polyurethane commonly employed for catheters with a Shore D hardness of 75 and 55 and Shore A 80

Component	Molar ratio	Molar ratio	Molar ratio
	Shore D 75	Shore D 55	Shore A 80
Polytetramethylene glycol Mn=650	1.0	1.0	
Polytetramethylene glycol Mn=1000			1.0
1,4-butanediol	3.5	2.9	1.3
4,4'-methylenebis(phenyl diisocyanate) MDI	4.5	3.9	2.3
50% stannous octoate in dioctyl phthalate catalyst	100 ppm		100 ppm
Properties			
T_g (°C)	35	-14	-48
Shear modulus (MPa)	500	70	10
Diffusion coefficient H_2O cm ² /sec	5E-9	1E-9	7E-7
Tensile strength (psi)			7,000
Elongation at break (%)			520
Mw (g/mol)	115,000		105,000
% water content at equilibrium	1.5	1.6	1.3

reendothelialization (skin regrowth). PU find use in nearly every facet of wound dressing, but are by no means the only material used for this purpose.

For flexible solid substrate, a thermoplastic material such as the Shore A 80 material defined in Table 11.1 is often used. Softer versions can also be employed by reducing the amount of hard segment in the formulation. In some cases, it is desirable to make a clear substrate through which the surface condition of the wound can be inspected without having to completely remove the dressing. For increasing film transparency, there are many means of proceeding including reducing hard segment, using an aliphatic hard segment, using polyester soft segment, mixing chain extenders, or processing in such a way to minimize hard segment phase growth [30, 31].

For nonocclusive dressings, the semipermeable component is sometimes a foam or nonwoven structure. There has been recent work on making nonwoven dressing by an electrosprayed process [32, 33]. Electrospray can make fibrous thread with very small diameter and allow addition of functional components during the spinning process. Conventional flexible PU foams used for comfort applications are not used for wound dressings because they do not provide adequate hydrophilicity to sufficiently absorb bodily fluids. This is overcome by maximization of the polyethylene glycol content in the foam soft segment [34]. The increased hydrophilicity also provides opportunity to act as a high surface area substrate for wound healing additives.

PU foam structures can be used for a wide variety of wounds but, because of their absorptive capacity, are primarily used in cases where a relatively large amount of fluid must be imbibed. Wounds where foam dressings are chosen are, for example,

burn sites, sutured sites, skin grafts, skin graft donor sites, and covering tube sites that transit through to the body exterior (i.e., tracheostomy). The foam is usually covered by a solid or air permeable film structure on the outside and a liquid permeable membrane facing the wound to prevent abraded urethane from entering into the wound. A negative pressure is sometimes employed by evacuating the foam structure through a solid-surfaced/airtight bandage covering. The partial vacuum draws the exudates into the bandage to more efficiently prevent festering [35].

Examples of PU foam hard segment are TDI–water, MDI–water, and various aliphatic structures. The soft segment is usually designed to provide the wetting interface either for the fluids or for specialized functional coatings. Common soft segment compositions are based on propylene oxide (PO) and ethylene oxide (EO), with EO reported to be as high as 75%. Froth foams have also been prepared for wound dressings using all polyethylene glycol soft segment, 1,4-butanediol (BDO), glycerine, and water as a chain extender/blowing agent and hexane diisocyanate for the polyisocyanate. The foaming is assisted by whipping large volumes of air into the reacting mass at elevated temperature and then allowing the blow reaction to expand the foam to its final potential. Such pads can be relatively soft, made at relatively higher densities, and are of course very hydrophilic [34].

Foam dressing size is also optimized for various functions. Foam pad thickness is usually in the range of 1.0–10.0 mm to optimize for capacity and facile attachment to the wound and surrounding skin. In contrast to a foam prepared for comfort where foam densities may be less than 2 lbs/ft³, a wound dressing density can be more than 6 lbs/ft³ to facilitate contact and wettability. The upper density is usually controlled such that the open-cell content is very high and the foam is not perceived to be hard.

Recent work has made electrosprayed nonwoven absorbent layers with commercial equipment specially designed to heat a molten polymer to a high enough temperature to reduce viscosity. Low viscosity is required so the TPU can exit a small orifice spinneret. Alternatively, the PU elastomer can be dissolved in a solvent at a concentration such that the viscosity is optimal for extrusion and removal of the solvent. Nonwoven absorbent TPUs have been reported electrospun from polymer melts [32]. With specialized equipment, this can be achieved using a standard TPU formulation. A TPU with Shore A 85 and composition by weight 60% PTMEG 1000, 34% 4,4'-MDI, and 6% BDO has been demonstrated to extrude fibers less than 10 μm in diameter. In contrast, a Shore A 97 TPU based on a polyester soft segment was dissolved at 10% (weight) in a 50/50 mixture of dimethylformamide and methyl ethyl ketone to electrospray fibers less than 1 μm in diameter [33]. A similar result was obtained by a 50/50 solvent mixture of dimethylformamide and tetrahydrofuran.

11.2.3 Bioabsorbable Polyurethanes

Volumes of PU used for medical implant applications requiring PU to be absorbed or degraded by the body are very small. However, about 10% of all patents filed in the biomedical PU field relate to tissue scaffolds, sutures, bioresorbable PU, or biodegradation of the PU. In addition, there has been steady patent activity in the field of PU hydrogels for medical applications. The concentration of this work in the past 5 years

may indicate that medical device manufacturers and doctors are perceiving that performance gaps in current materials can be filled with designed PU.

Degradation mechanisms *in vivo* are often consigned to hydrolytic, enzymatic, and oxidative processes [36]. In these applications, the standard TPU composed of 4,4'-MDI, BDO, and a polyether or polyester soft segment will be unacceptable. Part of the resistance is a result of biodegradation pathways that lead from the urethane bond to the formation of aromatic amines when using an aromatic polyisocyanate [37–39].

The highly specialized nature of applications requiring bioabsorbable PU removes many of the economic constraints associated with almost all other applications. In these applications, it is commonplace to copolymerize or transesterify two soft segment polyols to provide the optimum balance of material, biocompatibility, and degradation performance to achieve all requirements. The simple use of polyethylene oxide polyols or PO/EO block or random copolymer polyols is in principle doable from the perspective of biodegradability, but in fact is not usually employed [40]. PO/EO polyols can exceed 60% biodegradation in 10 days and up to 99% biodegradation in 28 days in the standard Organization for Economic Cooperation and Development (OECD) 301B test [41]. The test measures CO₂ evolution based on that predicted on the amount of carbon in the tested material. The microbial population can come from numerous sources, but a common one is from waste treatment plants. The level of degradation obtained by some polyalkylene glycols can normally be considered to result in nontoxic end products. Hydrolysis of the polyalkylene oxide chain is not commonly encountered (to produce two alcohols), but numerous studies have determined the ready oxidative and enzymatic degradation pathways for these materials [42, 43].

Aliphatic polyester polyols are also common substrates for designing biodegradable PU. Virtually, all polyester polyols are prone to hydrolytic mechanisms of degradation, as well oxidative and enzymatic mechanisms. This chemical susceptibility is usually disqualifying for applications where the urethane must be implanted and durable and has been demonstrated to result in extensive material degradation when used for those applications. On the other hand, this susceptibility makes polyesters the usual choice for maximizing the rate of biodegradation of a PU for which biosorption is desirable. Since the value-added aspects of optimum design outweigh most purely economic considerations, soft segment design usually reflects a balance of tensile performance, hydrophilicity, biodegradability, and processability (in cases where porosity or surface texture is desired).

For optimum hydrolysis and hydrophilicity, a semicrystalline polyester diol, based on the naturally derived chemical lactic acid to form polylactic acid (PLA), is usually explored (Fig. 11.6). With a large percentage of ester linkages, PLA is exceptionally susceptible to hydrolysis, but it also possesses forms having T_g of 65 °C and a crystalline melting temperature of 175 °C making it quite brittle [44, 45]. PLA can be, and often is, copolymerized or transesterified with other polyester polyols like polycaprolactone with more desirable material properties (apart from biodegradability) to make block copolymer soft segments having balanced properties (Fig. 11.7). Blends of TPU having a polyester soft segment with PLA have also been

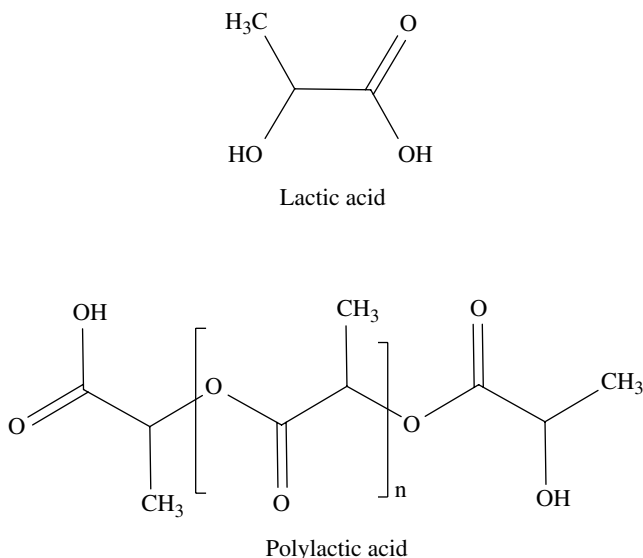


FIGURE 11.6 Structure of lactic acid and the derived biorenewable and biodegradable polymer polylactic acid (PLA).

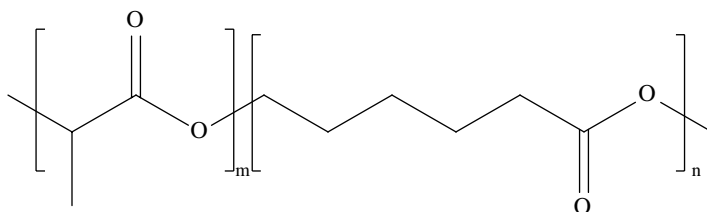


FIGURE 11.7 Copolymer of polycaprolactone and polylactic acid as might be prepared via transesterification.

demonstrated to have good physical properties and be capable of being extruded and injection molded into a scaffold for living tissue growth [46].

Hard segment design is also a part of developing biosorbable PU. Although it is certainly controversial, aromatic isocyanates are almost never used in these applications for fear of biodegradation resulting in carcinogenic aromatic amines such as toluene diamine or methylenedianiline [47]. Aliphatic diisocyanates have found some use in these applications due to their enhanced biodegradation kinetics. To be sure, this is largely a result of the lower glass transition temperature of aliphatic hard segments resulting in significantly higher water diffusion rates within the matrix. The more rapid degradation rate obtained with aliphatic isocyanates makes them less desirable for durable applications, but the measured faster biodegradation rate of aliphatic hard segments is established. Thus, there is substantial

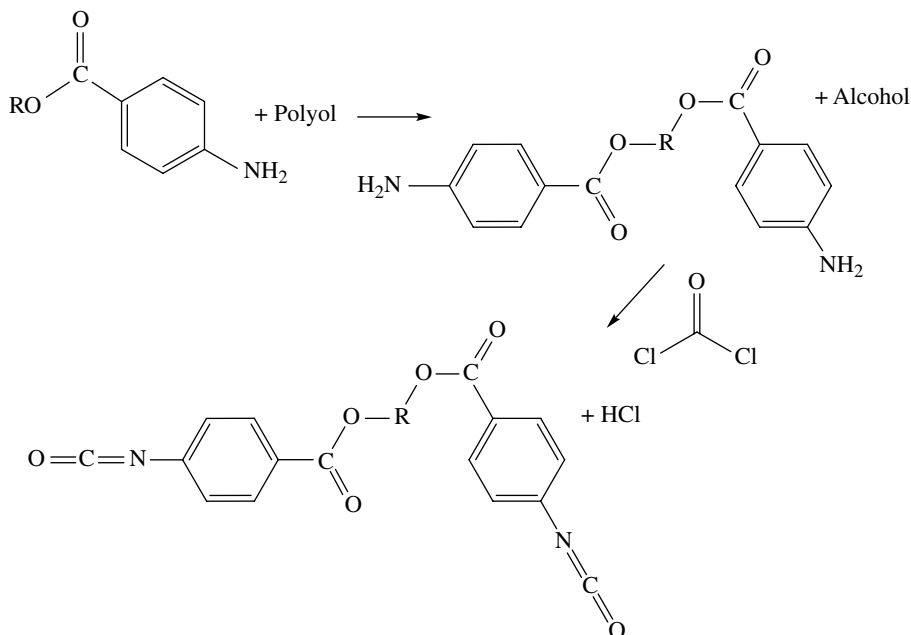


FIGURE 11.8 Preparation of a polyanilide and subsequent conversion to the polyisocyanate via phosgenation. Nonphosgene routes could also be considered (see Chapter 2).

literature associated with biosorbable materials prepared from relatively standard aliphatic hard segment structures.

The specialty nature of biosorbable materials has also spawned exploration of novel isocyanate structures for improved performance either from cell growth compatibility or biosorption standpoints. One class of aromatic isocyanates is based on polyisocyanate resulting from phosgenation of polyanilides. These materials can be prepared from commercially available polyols (ether or ester) and benzocaine (ethyl 4-aminobenzoate) followed by phosgenation (Fig. 11.8). It is believed that these structures can biodegrade into nonharmful side products while providing polymer properties of related polyanilide structures used for high-performance elastomers [48].

Since the conversion chemistry of amines to isocyanates (Chapter 2) can be generally applied, there are almost as many possible polyisocyanate structures as there are polyamines. One such structure is based on lysine—an essential dietary amino acid [49]. While lysine is extractable from foods, it is commonly available via fermentation with total available volumes of approximately 1 billion pounds per year. Although this availability makes it potentially attractive as a specialty chemical feedstock, difficulties permitting new plants for producing and utilizing phosgene can make any new isocyanate a daunting barrier to commercial entry. Figure 11.9 shows the structure of the lysine diisocyanate and its parent amino acid.

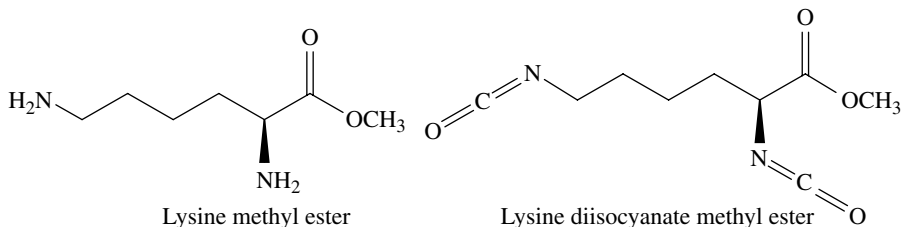


FIGURE 11.9 Structure of the polyamine lysine and the derived biodegradable polyisocyanate.

11.2.4 Hydrogels

Typical durable TPUs will absorb between 1 and 3% by weight water under ASTM conditions depending on PU composition. In contrast, some biomedical applications may require that a polymer matrix contain between 20 and 40% by weight water. Such applications may include soft contact lenses, wound dressing adhesive components, implant coatings, and media for drug delivery [50]. Polymer systems that can swell with water to this extent are often termed “hydrogels.” The design latitude that PU possess makes them effective hydrogel-forming polymers. A challenge for PU, and all polymers, is that the material must maintain substantial physical properties even when highly swollen. In addition, they should not present a fertile environment for microbial growth. Polyethylene glycol soft segments are commonly used in hydrogel design to provide hygroscopic base properties and a microbe resistant interface [51, 52]. PU chemistry also presents numerous design options for developing cross-links to buttress swollen polymer physical properties. Cross-linking agents may be relatively small like trimethylolpropane or diethanolamine. Alternatively, they can be higher-molecular-weight materials like ethoxylated glycerine. The hard segment for hydrogels is invariably aliphatic—usually hexane diisocyanate or isophorone diisocyanates (Chapter 2). The equilibrium water content and the physical properties are mutually dependent on chemistry and the degree of cross-linking.

Cross-link density in the swollen matrix is designed from the building blocks, but the actual molecular weight between cross-links must be determined empirically. A convenient method for calculation of cross-link density is the Flory–Rehner equation (11.1) based on measurements of equilibrium matrix swelling by a solvent [53]:

$$M_c = \frac{v_s d_p \left(V_p^{1/3} - \frac{V_p}{2} \right)}{\ln(1 - V_p) + V_p + X_{12} V_p^2} \quad (11.1)$$

In Equation 11.1, M_c is the molecular weight between cross-links, v_s is the molar volume of the solvent, d_p is the density of the polymer, V_p is the volume fraction of the swollen polymer in the solvent, and X_{12} is the polymer–solvent interaction parameter (see Chapter 4). As discussed in detail in Chapter 4, the interaction parameter can be calculated from Equation 11.2:

TABLE 11.2 Solubility parameters of representative solvents useful for determining cross-link density and molecular weight between cross-links for a polyurethane foam using the Flory–Rehner equation 11.1

Solvent (at 25 °C)	$\delta_s \frac{\text{cal}^{1/2}}{\text{cm}^{3/2}}$
Toluene	8.9
Acetone	9.9
1,4-dioxane	10
<i>N</i> -methyl pyrrolidone	11.3
Methanol	14.5

$$X_{12} = \frac{v_s (\delta_p - \delta_s)^2}{RT} \quad (11.2)$$

In Equation 11.2, δ_p and δ_s are the solubility parameters of the polymer and solvent, respectively. A discussion and table of solubility parameters useful for PU polymers can be found in Section 4.1. Solubility parameters for standard solvents relevant to measuring cross-linking in PU are found in Table 11.2 [54].

The cross-link density is calculated from Equation 11.3 following calculation of M_c from Equation 11.1:

$$d_c = \frac{d_p}{M_c} \quad (11.3)$$

Since the volume of PU used for hydrogels is inconsequential, the significance of this technology is the fundamental science it offers, the investment in future therapies consequential to human well-being, and as a signpost for future high-technology research in PU science. Activity on medical PU hydrogels is approximately 52 patents from 1990 to 2014. Only one company has filed more than two patents in this time, while over 500 articles in the open literature have been published.

11.2.5 Gloves and Condoms

While not high-technology medical applications, surgical/examination gloves and condoms represent about 10 million pounds of combined PU material volume. The two applications are about equal in size, and they are quite similar in technology. Additionally, both applications face varied competition from alternative polymer substitutes [55]. PU gloves in particular have growth potential resulting from substitution of non-PU latex products due to allergy concerns and powder coatings interfering with sterile operations [56].

The production process for medical gloves and condoms is quite similar, differing primarily in film thickness (glove thickness is about 120–150 μm, and condoms about 60 μm) [57]. The greater thickness of gloves also necessitates a coagulation step using calcium nitrate as a precipitant. The precipitant acts by substituting Ca²⁺ ions from the coagulant for Na⁺ ions in the dispersion, which initiates precipitation [58]. A simplified version of the dip procedure process for these materials is shown in Figure 11.10. A heated ceramic form or mold of the item is dipped into a bath of the PU dispersion. For thin films, a double dip is performed without coagulant. For a thicker film, a single dip is applied with the coagulant preapplied to the mold. The coated forms are then passed through a curing/annealing oven and then washed thoroughly of coagulants and migratory chemicals from the dispersion bath. There are many critical process parameters in this process including the cure step that has

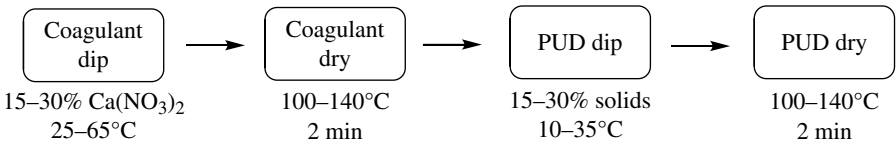


FIGURE 11.10 Simplified process flow for making medical films such as examination/surgical gloves from aqueous polyurethane dispersion.

TABLE 11.3 Composition of a polyurethane prepolymer/curative that could be made into a dispersion using procedures outlined in chapter 10 to subsequently make medical gloves

Component	Amount	Comment
2000 g/mol molecular weight polyether polyol, 88% PO, 12% EO triblock	52	Prepolymer component
425 g/mol molecular weight polypropylene oxide diol	14.7	Prepolymer component
4,4'-MDI 250 g/mol	29.1	Prepolymer component for higher modulus
50/50 4,4'-/4,2'-MDI 250 g/mol	4.2	Prepolymer component—lowers modulus slightly
230 g/mol molecular weight α,ω-polyoxypropylenediamine	16.8	Chain extender
Properties		
Tensile strength (psi)	3000	
Elongation at break (%)	780	High toughness
Stress at 100% elongation (psi)	200	Low stress at low elongations increases comfort
Tensile set	1%	Low deformation after donning

Full formulations will often include surfactant and biocide additives to aid processing and film formation.

significant influence on the final tensile strength, and the cleanliness of the form/mold that can affect the development of pinholes in the films.

An example polymer composition of a glove-forming material and properties is presented in Table 11.3. The preparation of the dispersion made from the components in Table 11.3 would be similar to that diagrammed in Figure 10.11.

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SPECIAL TOPIC: NONISOCYANATE ROUTES TO POLYURETHANES

12.1 GOVERNMENTAL REGULATION OF ISOCYANATES

The growth of commercial polyurethane building blocks and products is a testament to their efficacy and their efficiency. From the standpoint of both cost and processing, polyurethanes are attractive alternatives to many alternative thermoplastic and thermoset materials. The specificity of isocyanate reactivity with active hydrogen atoms, and the large number of available building blocks that have active hydrogen atoms, results in enormous potential for polymer innovation. However, this specific reactivity also makes isocyanate a potential hazard to living organisms ubiquitous with active hydrogen in living tissues and water [1–3]. Industrial consumers of isocyanates have adapted to the challenges associated with handling isocyanates by protecting workers from inhalation and skin contact. This is usually achieved by installing necessary and commonsense safeguards for worker protection [4]. However, the recent appearance of consumer products with unreacted isocyanates means that consumers, unregulated contractors, and also unknowing bystanders have the potential for unintentional primary exposure or incidental secondary exposure to isocyanates with the potential for harm. Occupational exposure has been documented to result in dermal and inhalation sensitization (rashes and asthma-like symptoms). Chronic exposure to isocyanates can additionally cause permanent harm to lungs, while of course acute exposure can in most severe cases be fatal [5].

In 2011, the U.S. Environmental Protection Agency (EPA) produced an action plan (RIN 2070-ZA15, April 20, 2011) for possible future regulation of methylene

diphenyl diisocyanate (MDI) and related compounds (4,4', 2,4', 2,2' isomers, polymeric MDI, and MDI dimers and trimers). The conclusion of the review resulted in the following action plan:

EPA intends to:

1. *Issue a data call-in for uncured MDI under TSCA section 8(c) to determine if there are allegations of significant adverse effects and initiate a TSCA section 8(d) rulemaking for one-time reporting of relevant unpublished health and safety studies for uncured MDI.*
2. *Consider initiating a TSCA section 4 test rule to require exposure monitoring studies on uncured MDI and its related polyisocyanates in consumer products and exposure monitoring studies in representative locations where commercial products with uncured MDI and its related polyisocyanates would be used.*
3. *Consider initiating rulemaking under TSCA section 6 for*
 - a. *Consumer products containing uncured MDI, and*
 - b. *Commercial uses of uncured MDI products in locations where the general population could be exposed.*
4. *Consider identifying additional diisocyanates and their related polyisocyanates that may be present in an uncured form in consumer products that should be evaluated for regulatory and/or voluntary action.*

The U.S. Occupational Health and Safety Administration (OSHA) has issued Directive Number CPL 03-00-017 (June 30, 2013) to initiate a National Emphasis Program “to identify or eliminate the incidence of adverse health effects associated with occupational exposure to isocyanates.” As mentioned earlier, occupational exposure to isocyanates in the developed economies, including the United States, is not previously a prominent issue, but the growing use of uncured isocyanate products may create a problem. OSHA “targets” for particular scrutiny are listed: general industry, construction, and maritime industries “where exposure to isocyanates are known or are likely to occur.”

Lastly, the State of California’s Department of Toxic Substances Control listed (March 25, 2014) spray polyurethane systems containing unreacted polyurethane (along with fire retardant tris(1,3-dichloro-2-propyl)phosphate and surface cleaners containing methylene chloride) as a priority product under the Green Chemistry Law of 2008. The covered materials for review include all isomers and mixtures of MDI (presumably including polymeric that contains MDI monomer), all isomers and mixtures of TDI, and hexamethylene diisocyanates (HDI). Other isocyanates or isocyanate trimers are specifically not included. While being listed as a priority product is not itself a ban, it is a step in the state process toward regulation. Promulgation of legal code could occur in 2016.

This activity follows the original activity of the European Commission (No. 552/2009 June 22, 2009) (and updated on May 25, 2011, to specify isomers) that

MDI shall not be placed on the market after 27, December 2010, as a constituent of mixtures in concentrations equal to or greater than 0.1% by weight of MDI for supply to the general market, unless suppliers shall ensure before the placing on the market that

the packaging: (a) contains protective gloves which comply with the requirements of Council directive 89/686/EEC; (b) is marked visibly, legibly and indelibly as follows and without prejudice to other Community legislation concerning the classification, packaging and labeling of substances and mixtures "Persons already sensitized to diisocyanates may develop allergic reactions when using this product. Persons suffering from asthma, eczema or skin problems should avoid contact, including dermal contact with this product....

With the governmental regulatory environment and the general European goal of using industrial solutions employing the least toxic effective components available, there has been increasing industrial and academic emphasis on obtaining urethane properties from systems that do not employ isocyanates. This chapter covers nonisocyanate chemistries that are actively explored for their potential to functionally substitute in polyurethane applications, regardless of economic barriers. The increased activity can be illustrated by analysis of the number of publications since 1990 on an emblematic non-isocyanate chemistry, reacting polycyclic carbonates and polyamines to make polyurethanes (Fig. 12.1). While the overall activity is relatively small, encompassing all publications academic and patent, the exponential increase is quite dramatic (Fig. 12.2).

Like many new areas where there is perceived to be an opening for acquiring intellectual assets, there have been numerous forays into patent space with concentrations particularly in the area of inks and toners. However, many of the patents represent the attempt to stake out a particular product based on specific material rather than representing a concentrated strategy.

While the attention paid to cyclic carbonate transformations to polyurethanes is the area of most prolific publication and patenting, other areas have also been

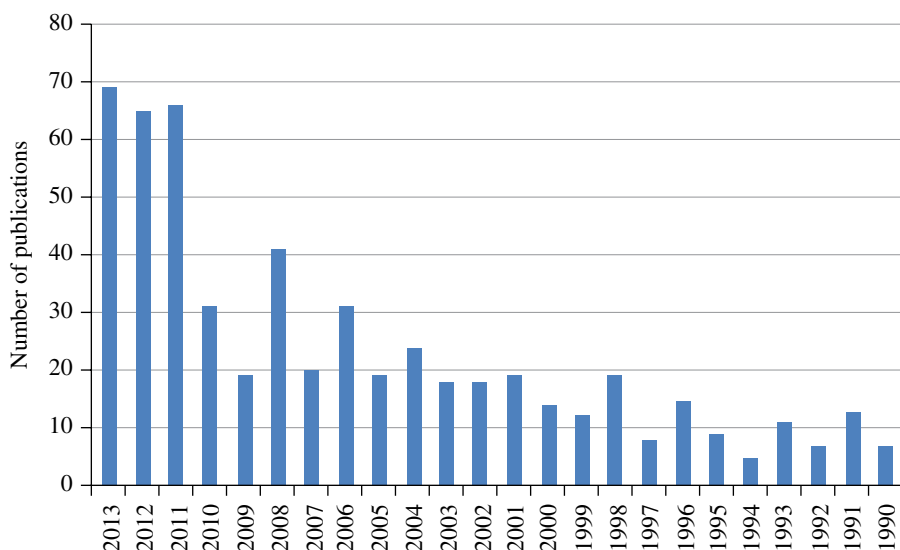


FIGURE 12.1 Growth in public documents exploring or protecting the production of polycyclic carbonates, their polymerization to polyurethanes, or their uses. Total = 635 references.

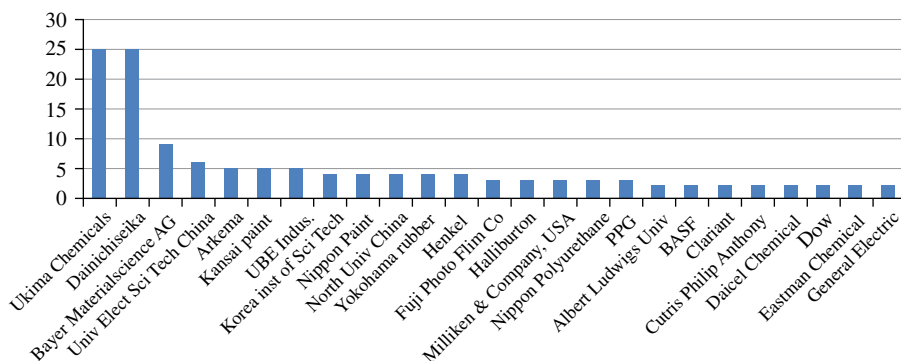


FIGURE 12.2 Patent activity of top filers of polycyclic carbonate to polyurethane technology. Total = 282 patents from 2000 to 2014.

developed using completely unrelated raw material and building blocks. These will be taken separately.

12.2 NONISOCYANATE ROUTES TO POLYURETHANES

There has been development of cross-linked and non-cross-linked chemistries advertised as nonisocyanate where an isocyanate is actually used in the chemistry and simply reacted prior to application. In this case, there is no isocyanate reaction subsequently involved in the final part fabrication. An example might be the reaction of diisocyanate with polyol and the subsequent reaction of a hydroxysilane to make a silane-tipped polyurethane backbone (Fig. 12.3a) [6, 7]. The final product in its use is isocyanate-free, but there was at some point an isocyanate in its construction. A similar situation can exist in the formation of acrylate-tipped hybrid polymer building block (Fig. 12.3b) [8, 9]. While these materials may be represented in some venues as “nonisocyanate,” this is simply a matter of semantics and is not the intent of this chapter. In this chapter will be presented synthetic routes to making urethane structures without ever employing isocyanate-based building blocks in their construction. The intent of such an exercise should in principle not replace one problematic building block (an isocyanate) with an equally (or more so) problematic substitute. In selective cases, such a result is achieved, while in others the substitution may be just another target for future regulation. Additionally, there is nonisocyanate chemistry based on blocked isocyanates (see Chapters 2 and 10) [10]. These are also isocyanates that are utilized in their urethane form reverting back to isocyanates upon heating. However, their “nonisocyanate” status is perhaps even more suspect.

12.2.1 Reactions of Polycyclic Carbonates with Polyamines

One route to polyurethanes without the benefit of polyisocyanate building blocks is via the reaction of polycyclic carbonates with polyamines [11–13]. As shown in Figure 12.1, research activity on this reaction is growing at an exponential rate. To

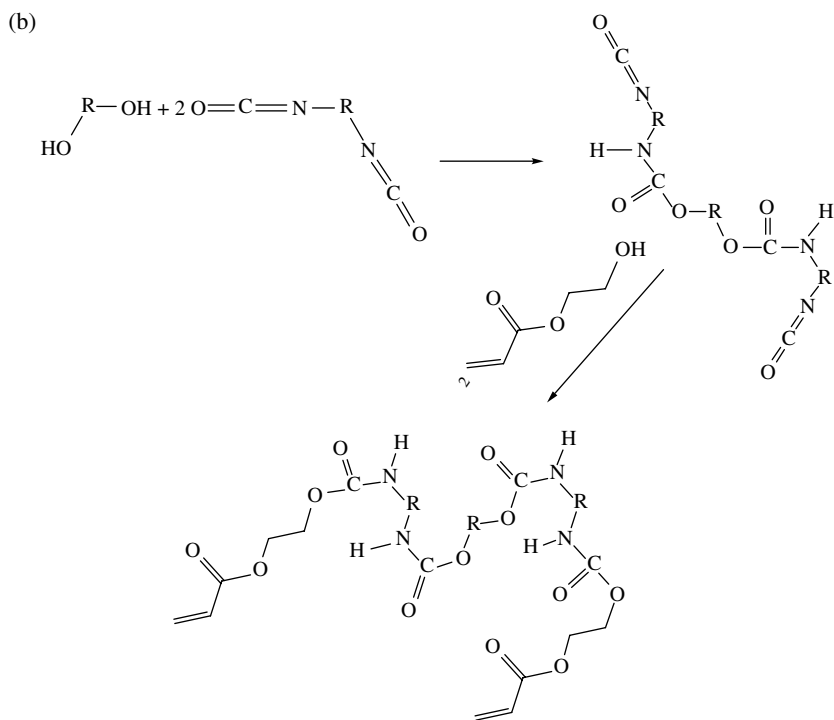


FIGURE 12.3 (a) A nonisocyanate containing final product with reactive end groups produced by hydrosilylation. (b) A nonisocyanate containing final product with acrylate end groups.

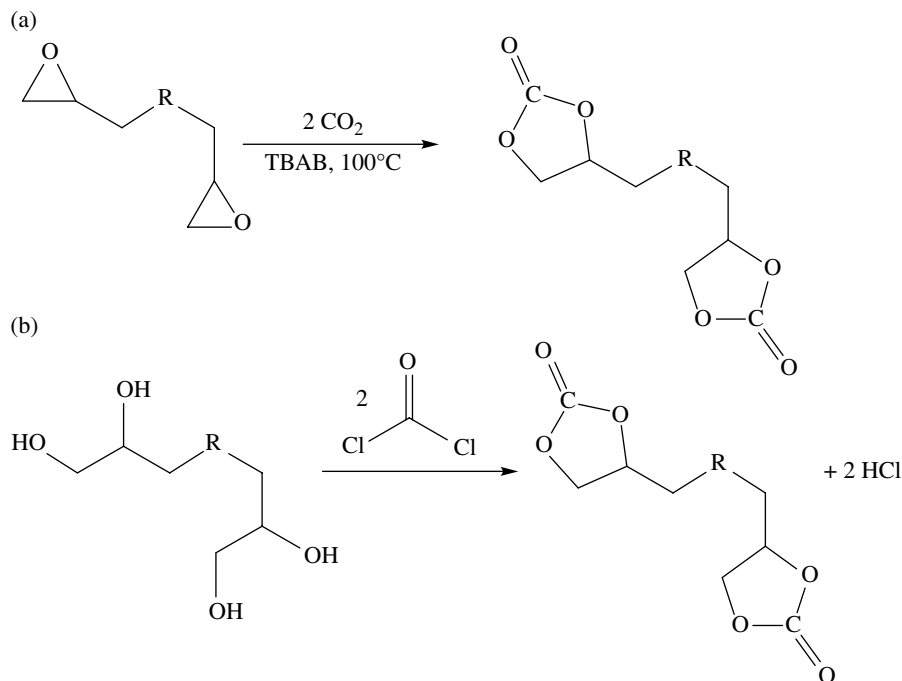


FIGURE 12.4 (a) Direct transformation of polyoxirane (epoxy) to polycyclic carbonate building block by CO_2 insertion and (b) by reaction of the hydrolyzed oxirane with phosgene.

some extent, this is due to availability of reagents and the relative ease of their transformation to polyurethane building blocks. Formation of cyclic carbonates is most easily achieved by the catalyzed reaction of an oxirane (epoxy) functionality with CO_2 (Fig. 12.4a). The transformation can also be performed using phosgene or triphosgene (Fig. 12.4b), as well from halohydrins or halogenated carbonates [14].

Figure 12.4a is the most prevalent route found in the literature and has been optimized to a great extent. Conversion temperatures are in the range of 25–150 °C, CO_2 pressures from 1 to 21 bar, and reaction times greater than 3 h. Reaction times and extent of conversion are a function of reaction conditions, oxirane substrate, and various cross-influences. Conditions for nearly quantitative selectivity and yield have been presented using heterogeneous catalysis under supercritical CO_2 conditions and extended reaction times. Conversion of polyoxirane to polycyclic carbonate is accompanied by a significant increase in viscosity that can be used to indirectly track conversion. Conversion of the oxirane to cyclic carbonate is also easily followed directly by FTIR (Chapter 5) with the disappearance of the epoxy ether at 800 cm^{-1} and the growth of the carbonyl peak at about 1780 cm^{-1} .

Polyurethane formation is achieved by reaction of polycyclic carbonate with polyamines having primary amine functionality (Fig. 12.5). The figure shows the

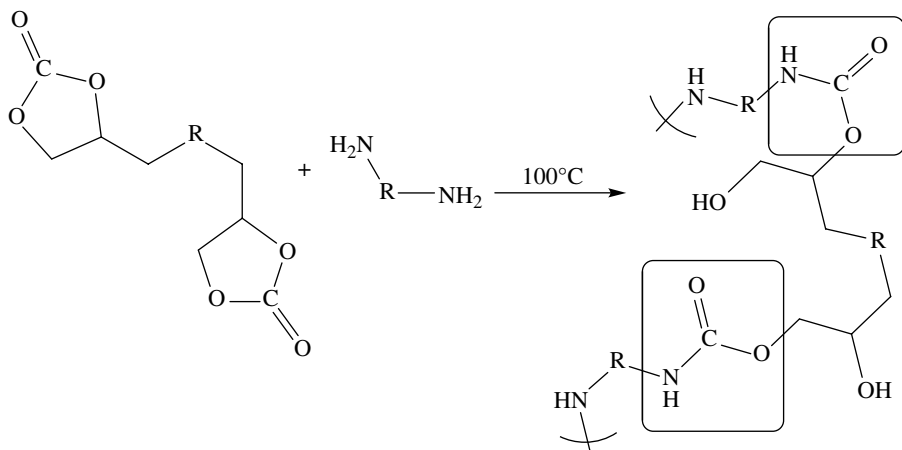


FIGURE 12.5 Illustrative reaction of a polycyclic carbonate with a polyamine to make a polyurethane. Boxes indicate the urethane group.

potential for ring opening to create either primary hydroxyl or secondary hydroxyl products. The ratio of primary to secondary hydroxyl formation along the backbone is driven by substituent groups on the ring [12]. In the presence of highly electron withdrawing groups, secondary hydroxyls predominate. As drawn in Figure 12.5, the ratio is approximately 1:1. The potential for intrachain hydrogen bonding between the backbone hydroxyls and the urethane carbonyls has been cited to bestow improved hydrolytic stability [13]. Evidence for this improvement is not yet presented in the literature.

It has been reported that cure of polyurethanes produced by reaction of cyclic carbonates and amines can occur at room temperature when allowed to proceed for extended times [13]. A similar experiment pursued with the parent polyepoxy and polyamine building blocks is not cured to the same degree, suggesting that electrophilicity of the carbonate linkage for the nucleophilic amine may predominate over ring strain promoting reactivity of epoxy moieties. As observed for conventional urethane synthesis, Lewis acids (such as tin octanoate) and Lewis bases (such as 1,8-diazabicycloundec-7-ene (DBU)) are very effective, but do not reportedly result in room temperature cure for normal processing times requiring heating to 70°C. However, while cyclic carbonates can be more reactive than epoxy functionality, they are by no means as reactive as isocyanates that exhibit diffusion-limited reactivity with amines. An additional influence on reactivity is the volume functional group density. This means that reactivity of building blocks to form polymer will be influenced by the equivalent weight of the reactive components with lower equivalent weight translating into higher reactivity. This is primarily an influence of the exothermic ring-opening reaction and the activation energy of reaction.

A related reaction of aziridines with CO₂ can lead directly to polyurethanes (Fig. 12.6). This reaction can result in formation of a urethane-amine with the relative ratios affected strongly by polymerization conditions [15–17]. The urethane

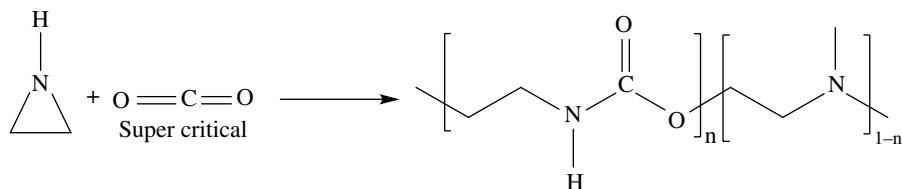


FIGURE 12.6 Illustrative reaction of aziridine with super critical CO₂ to make a polyurethane amine.

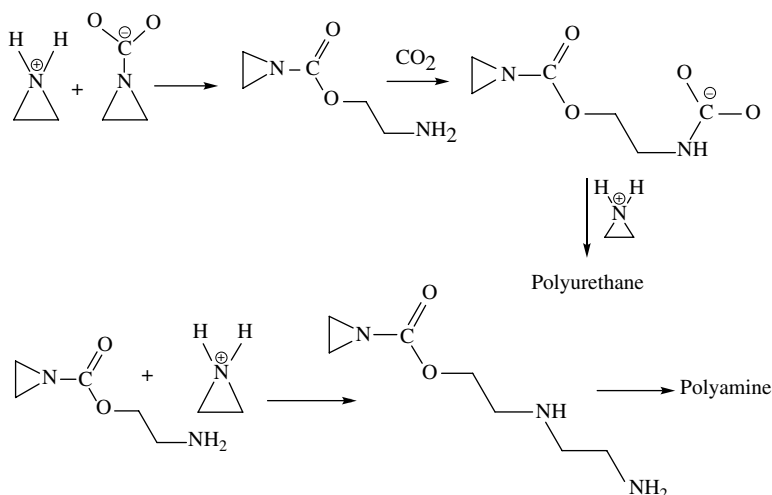


FIGURE 12.7 Two potential mechanisms for formation of the polyurethane-amine backbone from aziridine polymerization with CO₂.

formation reaction occurs via nucleophilic attack of the carbamate anion on the aziridinium cation. The competitive reaction forming the polyamine can occur via ring opening of the aziridinium cation by the primary amine (Fig. 12.7).

Industrial and commercial adoption of cyclic carbonate chemistry for making polyurethane backbones will depend on several factors: (i) the ability to make useful materials, (ii) the ability to make those materials economically, and (iii) the environmental, health, and safety advantage relative to isocyanate-based urethanes [18–21]. The following analysis for polycyclic carbonate–amine reaction would apply equally to each other pathway discussed herein.

Taking each factor into consideration:

1. In principle, cyclic carbonate chemistry can be nearly as flexible as polyurethane. While it would appear that polycyclic carbonate chemistry is less able to form phase separated materials, it may be possible to create hard block/soft block polymer structures as made in polyurethane chemistry. This could be

achieved by employing high-molecular-weight soft segment diamines and preparing hard segments from cyclic carbonate reactions with very low equivalent weight chain extenders such as ethylenediamine. The ability to form intrahard segment hydrogen bonding might create sufficient cohesive energy density to result in a durable physical cross-link. With sufficient phase volume, it may be also possible to create a cocontinuous structure within the elastomer and observe traditional polyurethane tensile properties. However, it remains to be seen if the components can produce the required reaction-induced phase separation prior to gross phase separation of the reacting components due to reactivity, viscosity, and solubility differences between the components. A possible solution for this may come by preparation of polycyclic carbonate–polyamine prepolymers. Prepolymer preparation prior to making the hard segment may provide adequate compatibilization to maintain a homogeneous initial state from which microphase separation into hard and soft segments can occur. Additionally, due to the relatively slow reactivity of polycyclic carbonates and incompatibility with blowing agent technology, this technology may not be suitable for flexible or rigid foam purposes.

2. Polyisocyanate prices are generally less expensive than polyoxirane (epoxy resins) due to fundamental costs associated with industrial manufacture. The price difference is as much as 30%. Subsequent addition of CO₂ to epoxy resin will further increase differential cost depending on the process chosen, the reaction time, the need to purify/separate products, and the volume produced. In addition, the cost of polyamines is highly variable but substantially more expensive than polyether or polyester polyols. The difference can be 100% or more. Thus, it can be anticipated that the cost of a polyurethane elastomer produced by reaction of a polycyclic carbonate with polyamines may be as much as twice more expensive as the same elastomer produced by isocyanate-based chemistry. This may not be the dominant factor if regulatory agencies decide that the risks of polyisocyanates outweigh the benefits.
3. The cost/benefit ratio will require that polyamines employed making nonisocyanate polyurethanes are substantially less problematic than polyisocyanates [22–24]. While the relative toxicity of any particular polyamine relative to a particular polyisocyanate will depend on numerous structure–property relationships, it is unavoidable that amines are strong bases and are therefore dangerous by skin contact and inhalation. It will remain to be seen if the potential benefits of this nonisocyanate route to polyurethanes can withstand a health and safety examination on the same grounds.

12.2.2 Direct Transformations of Amines to Urethanes

Section 2.2.1.2 presents nonphosgene routes to isocyanates by reactions of amines with dimethyl carbonates. In that process, isocyanate is created without phosgene but rather obtained by reversion of urethane to an isocyanate and an alcohol. In that method, the point is to obtain an isocyanate without employing the dangerous

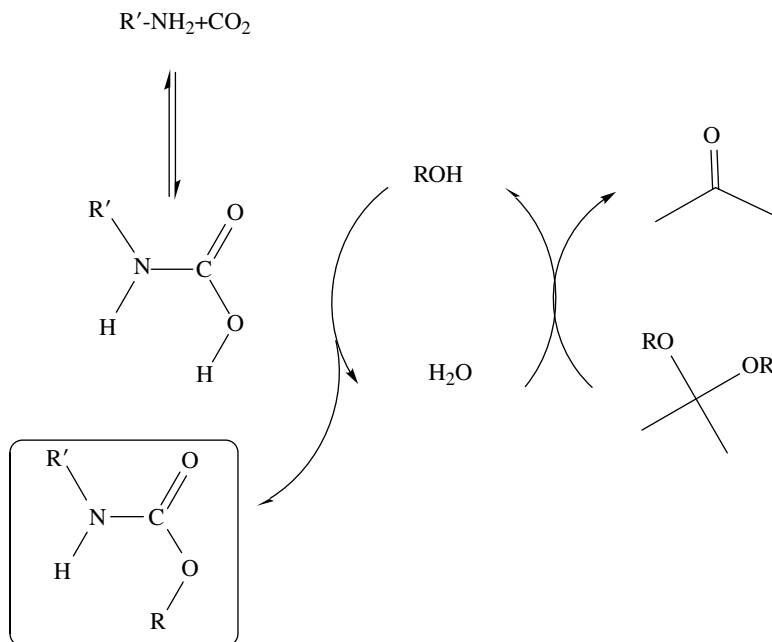


FIGURE 12.8 Conversion of amine to carbamate by reaction with CO_2 and subsequent reaction with an alcohol. Polymers can be formed when the amine is a polyamine and the alcohol is a polyol. Box indicates the urethane product.

phosgene reagent. Work along these lines has also produced urethane functionality without isocyanate, which in principle can be extended to produce polyurethanes via simplified reaction and reagent choices.

One such route converts amines, alcohols, and CO_2 directly to urethanes [25–27]. The reaction is catalyzed and performed at elevated temperature and pressure (Fig. 12.8). Given the instability of the carbamic acid and the relative reaction rates, it is possible that this reaction actually proceeds through an isocyanate intermediate before forming the urethane. The reaction has been optimized to produce high yields and selectivities, however; reaction times tend to be long. The use of mixed polyamines and polyols offers the potential to produce polymers with hard segments.

A related mechanism employs an onium salt (in the illustration case of Figure 12.9 an ammonium salt) with an alkyl halide to produce a urethane group [28]. As before, the use of mixed polyamines and alternative alkyl halides offers the potential for polymerization and design flexibility.

Beginning with the same first step, urethane has also been produced with good yield and milder conditions using Mitsunobu's reagent [29, 30]. The relatively easier reaction conditions are partially offset by consumption of the reagent, making the reaction potentially expensive (Fig. 12.10). In fact, all reactions transforming amines to urethanes by reaction with CO_2 , and a source of organic moiety to reduce the carbamic acid to the urethane, involve the loss of reagents and the need to separate the

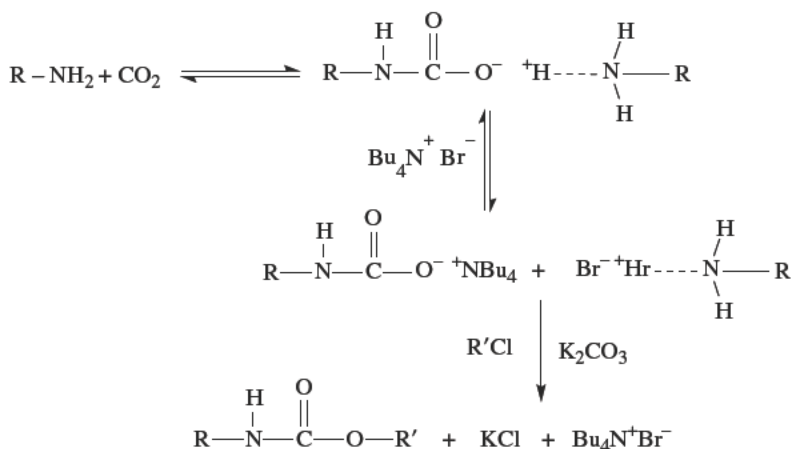


FIGURE 12.9 Reaction of an amine with CO_2 to make urethane via an onium salt complex. Polymer can be formed when a polyamine is employed and R' is capable of transesterification.

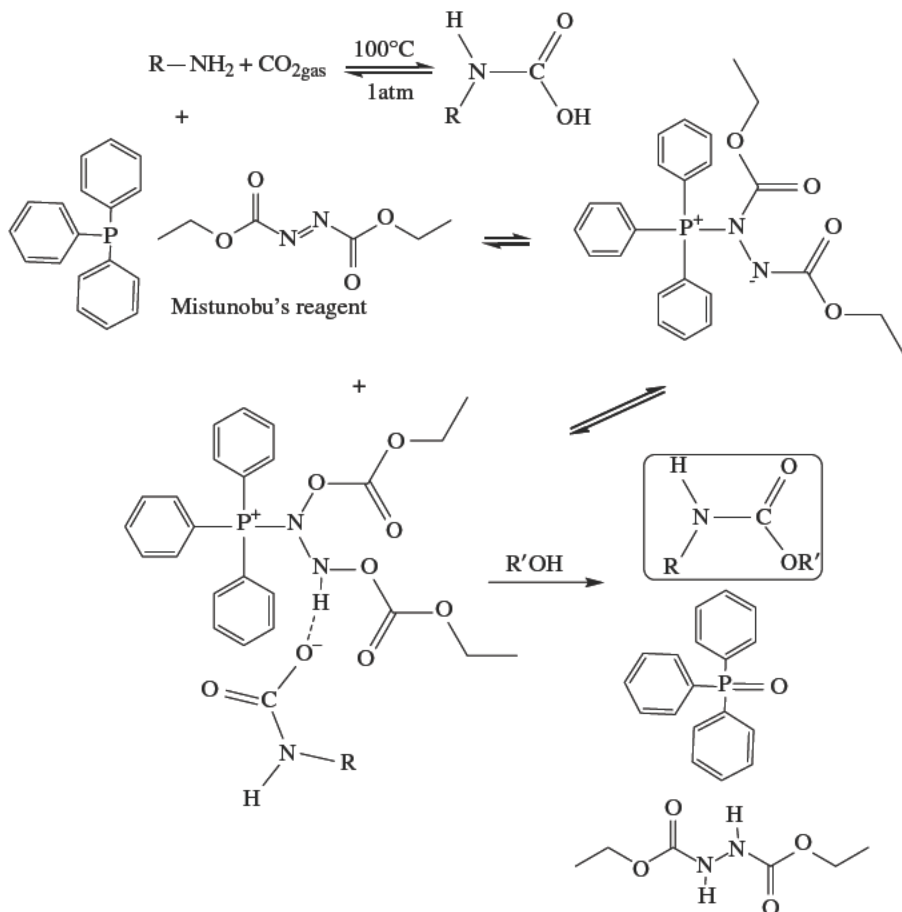


FIGURE 12.10 Reaction of amine with CO_2 to form urethane using Mitsunobu's reagent. A polyurethane can be produced when a polyamine is employed.

desired urethane from these compounds. Like the reactions of cyclic carbonates and amines to form urethanes discussed in the preceding section, conversion of amines and CO_2 to urethanes employs reagents with potentially troublesome safety profiles, but in this case, the materials are consumed in the industrial manufacturing step and would not provide a possible route of amine exposure to consumers or unregulated contractors.

12.2.3 Reactions of Polycarbamates

Carbamates can be prepared by reaction of alcohols with other carbamates or by reactions of alcohols with urea [31]. The simplest carbamate is methyl carbamate and is prepared by reaction of methanol with urea (Fig. 12.11). The carbamate can be subsequently reacted with a single aldehyde to produce a hemiaminal or with two

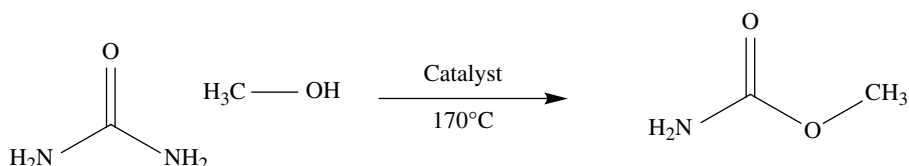


FIGURE 12.11 Reaction of urea and methanol to form methyl carbamate.

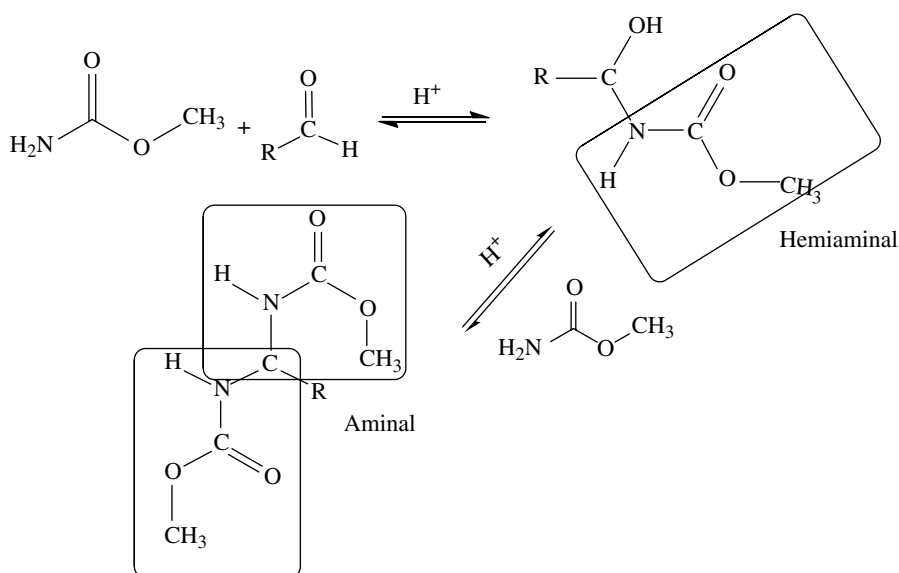


FIGURE 12.12 Reaction of methyl carbamate and formaldehyde to make the hemiaminal and subsequently the aminal. Polyurethane can be formed when a polycarbamate and a polyaldehyde are reacted together. Boxes indicate the urethane groups.

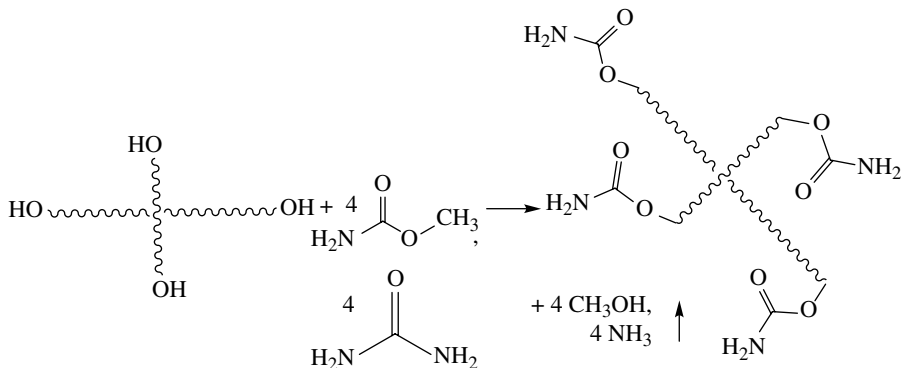


FIGURE 12.13 Reaction of a polyol with methyl carbamate or urea to produce a multifunction polycarbamate that can form a cross-linked polyurethane when reacted with a polyaldehyde.

aldehydes to produce an aминаl (Fig. 12.12). As noted in an early patent, the initial reaction with methanol can be equally performed on a polyol to produce a polycarbamate (Fig. 12.13), which can be subsequently reacted with a polyaldehyde to create a three-dimensional polyurethane cross-linking structure [32]. The catalyzed reaction can proceed at room temperature that makes the reaction particularly suitable as a potential replacement for some isocyanate-derived products. While formation of the aминаl is possible in controlled small-molecule model studies, it is less common for addition polymerization making cross-linked polyurethane where hemiaminal formation predominates.

The range of potential polycarbamate building blocks via aминаl chemistry is limited only by imagination since the number of possible polyol reagents is immense and the urea feedstock is relatively cost-effective. On the other hand, the number of polyaldehydes is relative small and therefore potentially expensive. Furthermore, aldehyde propensity to oxidize in the presence of oxygen is a potential complication and must be accounted for in reactant stoichiometries in a similar manner that MDI dimerization must be accounted for in preparation of MDI-based foams.

12.2.4 Conversion of Hydroxamic Acids to Polyurethane

Conversion of diesters to dicarbamates via formation of the hydroxamic acid is a relatively seldom traveled route to polyurethanes. In part, this is surely because the synthesis is somewhat laborious with relatively modest yield. In part, it may also be because the route to urethane via hydroxamic acid is actually through an isocyanate intermediate. The reaction begins with displacement of the methyl ester with the hydroxamic acid by reaction with hydroxylamine hydrochloride (Fig. 12.14). The hydroxamic acid is converted to isocyanate by Lossen rearrange-

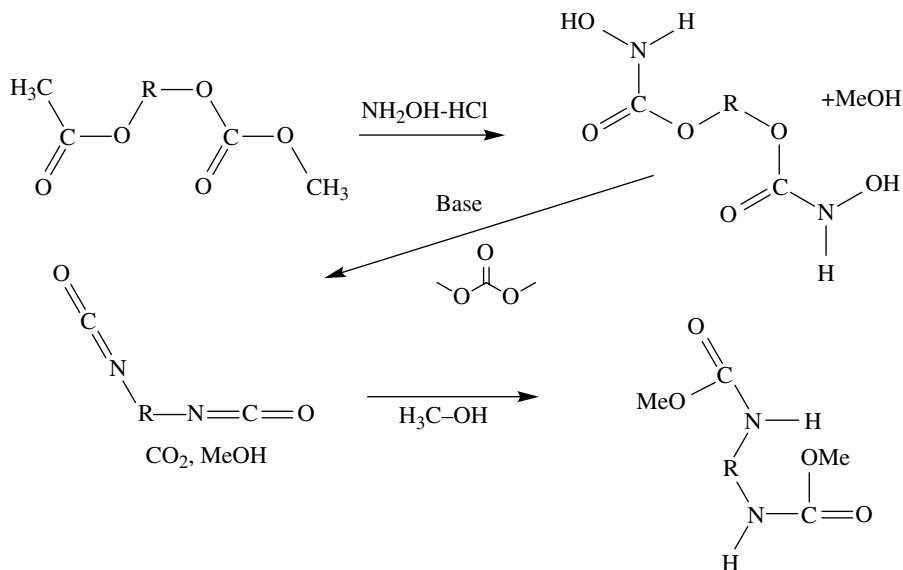


FIGURE 12.14 Reaction of a dimethyl ester with hydroxylamine hydrochloride to form the dihydroxamic acid, which through subsequent reactions forms a dicarbamate. Reaction of the dicarbamate with a polyol can form high-molecular-weight polyurethane.

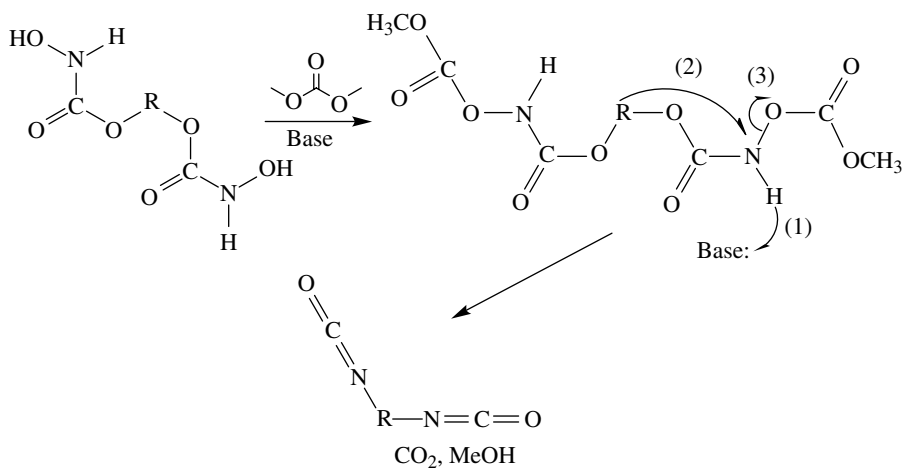


FIGURE 12.15 Reaction of the polyhydroxamic acid with dimethyl carbonate resulting in a latent polyisocyanate through the Lossen rearrangement.

ment (Fig. 12.15). Rapid reaction with methanol leads to the bis-carbamate [33, 34]. Subsequent reaction with a polyol results in the polyurethane polymer. High-functionality polyols and diesters of varying molecular weights can result in block copolymer formation.

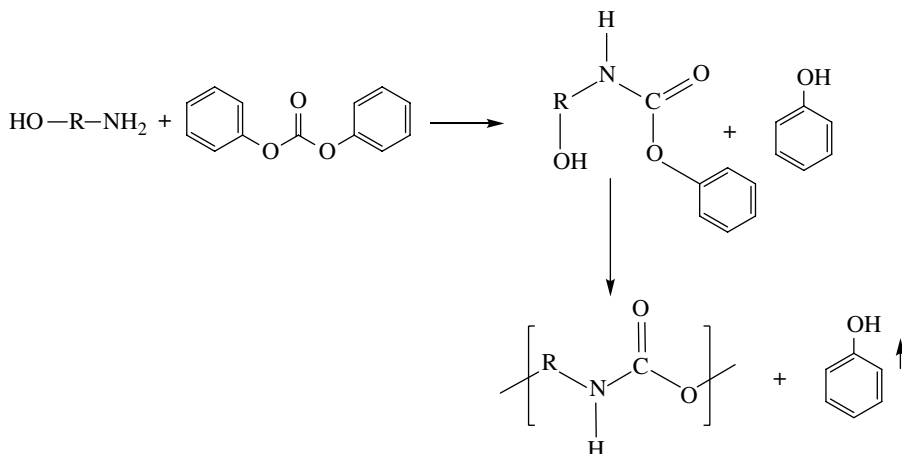


FIGURE 12.16 Illustrative reaction of hydroxylamine and diphenyl carbonate forming polyurethane with phenol by-product. Removal of the phenol is required for attaining high molecular weight.

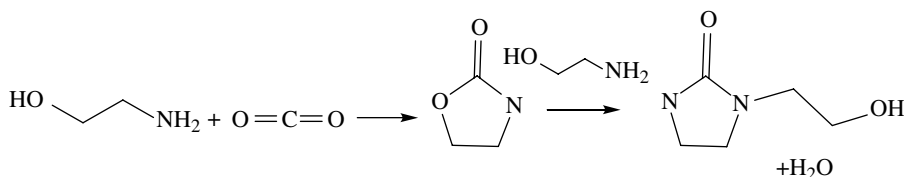


FIGURE 12.17 Direct reaction of ethanolamine and carbon dioxide to form oxazolidinone and subsequent reaction with ethanolamine to form hydroxyethyl imidazolidinone. This side reaction can be avoided by using higher-molecular-weight alcoholamines or having branched structures that inhibit intramolecular cyclization.

12.2.5 Conversion of Hydroxylamines to Polyurethanes

The conversion of hydroxylamines to urethanes and polyurethanes has been described in the literature [27]. The carbonyl of the carbonate linkage provides a ready coreactant for the hydroxylamine, and high molecular weights have been reported using this procedure (Fig. 12.16) with removal of the phenol coproduct and design of the R group to inhibit formation of the cyclic urethane. The cost of diphenyl carbonate, its high unit ratio, and the large volume of phenol coproduct could be an inhibiting factor in implementation. An alternative direct reaction of phosgene or CO_2 with hydroxylamines would yield mixed cyclic products like 2-oxazolidinone or hydroxyethyl imidazolidinone (Fig. 12.17) or mixed urethane/carboxylate chain functionality due to the reactivity of both amines and hydroxyls for the electrophilic carbonic acid derivatives depending on initial reagents.

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INDEX

- acrylic polyol, 13, 14, 44, 360, 361, 367, 371
 - preparation, 45–7
- adhesives, 339–53 *see also* hotmelt adhesive; polyurethane dispersion (PUD); radiation (Rad) cure adhesive; reactive hotmelt adhesive
 - applications, 339–42
 - commercial dynamics, 340
 - component usage, 340, 341
 - consumption, 339–41
 - format, 341–2
 - growth, 338
 - market dynamics, 340
 - one-part, 342, 344–5
 - standard tests, 342–3
 - trends, 350–353
 - two-part, 344
 - volumes, 338
- aliphatic isocyanates, 63, 81–9, 107, 123, 384
 - applications, 86–9
 - in coatings, 355, 356, 359–60, 368–70
 - markets, 82
 - production by non-phosgene routes, 87–8
- allophonate, 61, 62, 117–19
 - reversion, 118
- amides (formation of from isocyanates), 122–3
- aniline, 62–3, 73–8, 86, 114, 117
- AP6, 79
- APA, 79, 80
- appliance foams, 36, 276–81
 - blowing agents, 280–281
 - formulations and properties, 277–9
 - reverse heat leakage (RHL) test, 277, 280–281
 - similarities to PIP foams, 276–7
 - trends, 280
- aromatic polyesters *see* polyesters
- Asia(n)
 - elastomer market, 295–8
 - flexible foam consumption, 236
 - rigid foams, 256, 257
 - seating foam preferences, 246
 - supply/demand ratio, 257
- Association of Home Appliance Manufacturers (AHAM), 277
- ASTM, 161

- atomic force microscopy (AFM), 131,
168–9, 173–6
- autocatalytic polyols, 223, 266
- automotive *see* transportation
- autotitration, 162
- BASF SE, 2, 32, 249, 251, 252, 258,
287–90, 307, 315, 351, 369–70, 376
- Bayer AG, 2, 69, 249, 251, 258,
287–90, 307, 315, 351, 369–70,
376, 377, 379
- Bayer Otto, 1
- binodal *see* nucleation and growth
- bioabsorbable polyurethanes
degradation mechanisms, 383
design criteria, 383–4
standard test for, 383
structure/property relationships, 384–5
volumes, 382
- biuret, 61, 62, 69, 119
- block copolymers, 23, 26–7, 128–34, 243,
300, 306, 319, 342, 383, 405
phase diagram, 134
phase structures, 132–9, 175
- blocked (or protected) isocyanates, 119,
123, 342, 345, 356, 365–7, 395
- blowing agents, 8, 208, 237, 251, 268,
270, 272, 277, 280–284, 301,
382, 400
global warming potential, 282
ozone depletion potential, 282
patent activity, 288–9
phase-out schedule, 282–4
substitution, 284
structures and properties, 282
- Bostik, 351
- Boyle's law, 150
- Bragg equation, 136, 179
- Bruker nano-surface, 174
- bubble nucleation, 218–19
- Budiansky equation, 140–141
- butylene oxide, 12, 17, 262
via chlorohydrin, 14
- California, Department of Toxic Substance
Control, 265, 393
- carbodiimide, 69, 79, 112, 120–122
trimerization, 121
- Carothers equation, 32
- cast elastomers
applications, 314
cast vs. thermoplastic elastomers,
294–5
classifications, 356
commercial relationships,
308–9, 359
footwear, 300–301
molding, 312–13
prepolymer systems, 309
systems houses, 308
- castor oil, 55, 251–2, 364
- catalysts
amines, 110–111, 317
base, 16, 23–5, 107
blow/gel ratio, 111
DMC, 8, 16, 20–24
design considerations, 224
foaming, 223–4
mechanism, 33, 107–12
Lewis acid, 108–10
metal alkoxylate, 33, 110, 251, 317
phospholene oxide, 120–122
reactive, 8, 223–4, 225
regulation of, 251
structures, 108
trimerization, 111–12
- catheters, 377–80
alternative materials, 378
design criteria, 380
formulation and properties, 381
infection susceptibility, 379–80
volumes, 377
- cell anisotropy, 272
- chain extenders, 10, 51, 89–95, 128, 213,
222, 223, 301, 305, 308, 309, 324,
328, 344–5, 348–9, 361, 362, 364,
381, 382, 400
structures, 93–5
- chi parameter *see* Flory interaction
parameter
- China(ese)
demand, 237, 257
and European market, 258–9
growth, 11, 235–7
manufacturing, 7, 236, 299–300, 315,
323, 351
patent activity, 249, 287–9, 377
TDI use and production, 63

- coalescence, 17, 135, 212, 218, 348
coatings, 353–71 *see also* polyurethane
 dispersion (PUD) coatings, powder
 coatings; Radiation (Rad) cure
 coatings; solvent borne coatings
 architectural vs. industrial, 354
 ASTM conventions, 356–7
 binder, 336
 components, 336
 consumption, 338, 354
 formulations and properties, 359–68
 markets, 353–5, 359
 segmentation, 337, 338
 technology segmentation, 355
 testing, 355–8
 trends, 368–71
 volumes, 337, 338
cohesive energy density, 91, 131, 147, 328, 345, 400
Coim Corporation, 32, 315
comfort factor, 8, 217, 239
commoditization, 12, 36, 63, 69, 296
construction foams, 36–7, 111, 260–276
controlled polymerization rate (CPR), 164–6
copolymer polyol(s), 8, 48–51, 212, 215, 217, 228, 383
 grafting, 49
correlation function *see* small angle x-ray scattering
critical hard segment length, 138
crosslink density, 148, 243, 261, 386–7
 calculation of, 386–7

d-spacing *see* small angle x-ray scattering
Davies equation, 139–42
de-mold expansion, 36
derivitization and titration, 162–4
differential scanning calorimetry (DSC), 169
diisocyanatodicyclohexylmethane *see* H₁₂MDI
di-methyl carbonate, 42–3
 azeotrope with methanol, 43
distributors, 247, 249, 308–9, 315–16, 359
DMC catalysts *see* catalysts
Dow Chemical Company, 2, 249, 258, 307, 351, 369, 376
Dupont de Nemours, E. I., 2, 346, 369, 376

dynamic mechanical analysis (DMA), 114–15, 168, 195–9
 fixtures, 198–9
 rheokinetic measurement, 198–9
 vs. tensile analysis, 195–6

elastane *see* elastomeric fiber
elastic fiber, 323–8
 consumption, 323–4
 fiber spinning, 324, 328
 global manufacturing, 323
 growth, 296
 hard segment, 324, 327
 markets, 323
 and MDI, 79
 pricing, 296, 324
 production, 8, 323–4
 trends, 328
elastomer(s) *see also*; cast elastomers;
 footwear; reaction injection molding (RIM); spray; thermoplastic elastomers
 applications, 307–8
 consumption, 296–8
 markets, 295–8
 patent activity, 329–31
 segmentation, 297–8, 308
 trends, 328–31
epoxidation and ring opening, 55
equivalent box model, 145, 147
ethylene oxide, 12, 15–17, 23, 24, 27, 211, 382, 383
Europe(ean)
 Commission, 393
 flexible foam consumption, 236
 footwear production, 299–300
 prepolymer preferences, 309
 production in Eastern vs. Western Europe, 258
 regulation, 237, 251, 283
 rigid foam consumption, 256, 258, 276, 284
 seating foam preferences, 246, 248
Exxon, 63

Farben, I. G., 1, 2
Fick's law, 137
films, 81
flame retardant(s), 8, 12, 36, 208, 237, 241, 251, 261, 272, 289

- Flory interaction parameter, 131–4, 156, 219
Flory Rehner equation, 386
Flory-Schultz distribution, 37
foam *see also* molded foams; rigid foams;
 slabstock foams
 “blow-off” 218–19, 243
 bubble nucleation, 218–19
 comfort factor, 239
 design considerations, 221–2
 formulation screening, 219–20, 223, 228–9
 hysteresis, 143, 195, 248, 250–251, 304
 “low-resilience”, 241
 open vs. closed cell, 149–51, 220
 processes, 217–22
 rheology, 229
 sag factor, 239
 “scorch”, 209
 “sigh back”, 229
 structure/property relationships, 221–22,
 228–33
 “tight” foams, 219
footwear, 299–307
 adhesives, 340
 design concepts, 304
 formulations and properties, 305, 306
 markets and other polymers, 300–301,
 306–7
 polyester vs. polyether systems, 301–2
 processing, 302
 prepolymer and quasi-prepolymers
 systems, 302
 shoe soles, 301
 Shore-A requirements, 302–3
 standard tests, 303
 trends, 307
formaldehyde, 75
Formosa Chemical and Fiber Corp., 63
Fox equation, 152–4
froth foams, 267–70
 advantages over spray foams, 267–8
 comparison of spray and froth foam
 properties, 271
 handle and static mixer, 268–9
 product delivery, 268–9
 formulations and properties, 269–70
furniture, 238–45 *see also* mattresses and
 bedding
 foam design considerations, 238–9
 formulations, 239
 markets, 239–41
 regulation, 241
FTIR, 106–7, 120, 164–5, 176–81
 resonance assignments, 120, 177–9
gamma distribution *see* Flory-Schultz
 distribution
gas-phase phosgenation *see* phosgenation
Ginzburg-Sonnenschein equation, 154–5
glass transition temperature(s), 144–5,
 151–6, 198, 243–4
global warming potential (GWP), 281–2
gloves and condoms, 387–9
 formulation and properties, 388
 production and processing, 388–9
 volumes, 387
Gordon-Taylor equation, 153–5
“green strength”, 345
 H_{12} MDI, 82
H. B. Fuller, 351
Halpin-Tsai equation, 141–2
hard segment, 89–90, 128, 129, 132–4, 136,
 138–48, 154–5, 169–72, 175, 179,
 182–5, 200–202, 211, 215–17, 219,
 231, 309, 317–19, 324–28, 345, 361,
 364, 381–2, 384–6, 400–401
 hydrogen bonding within, 91–2, 182
hotmelt adhesive, 339, 340, 345–6
 formulation and properties, 346
HPO process, 12, 14, 15
Huafeng Group, 32
humid aged compression set (HACS), 229–32
humid aged load loss (HALL), 231–3
Huntsman Corp. 258, 315, 369, 376
hydroformylation and reduction, 56–8
hydrogels, 386–7
 applications, 386
 design criteria, 386
 effect of crosslink density, 386–7
 patent activity, 387
hydrogenation of nitrotoluene, 67
hydroxyl number, 161–4
hysteresis, 195
infra-red spectroscopy *see* FTIR
Instron Corp., 189, 193
indentation force deflection (IFD), 238, 240
insulation *see* thermal insulation

- isocyanate testing, 166–8
- isocyanurate(s), 29, 34, 86, 111–12, 180
 - see also* polyisocyanurate foams
- isophorone diisocyanate, 82, 85, 88, 386
- Japan(ese), 73, 88
 - coatings, 338–9
 - growth, 235, 237
 - patents, 329, 351–2, 370–371
- Kerner's equation, 138–9, 142
- Knudsen effect *see* thermal insulation
- Kokai patent publications, 351, 370
- Kwei equation, 155–6
- Latin America
 - flexible foam consumption, 236, 237
 - elastomer markets, 296, 298
- Lu-Weiss equation, 156
- Lubrizol Corp., 315
- lysine diisocyanate, 385–6
- 3M Corporation, 351
- macromers, 49–51
- mannich polyol, 13, 266–8
- markets and marketing
 - automotive, 8
 - vs.* commercial activities, 6
 - construction, 8
 - market followers, 240–241, 251
 - “tightening”, 7
- Martin, Roth, Stiehler equation, 148
- mattresses and bedding, 241–5 *see also* viscoelastic foams
 - foam quality and performance, 241
 - structure, 241
- medical uses, 375–91 *see* bioabsorbable
 - polyurethanes; catheters; gloves and condoms; hydrogels; wound dressings
- growth, 376
- markets, 375–7
- volumes, 375–6
- Medtronic Corp., 376–8
- methylene bisphenyldiamine (MDA)
 - oligomerization, 77
 - production, 76–7
- methylenebis (phenylisocyanate) (MDI)
 - analysis, 166–8
 - dimerization, 79–80, 82, 119
 - growth, 63
 - monomer, 79, 324
 - photooxidation, 82–3
 - process control, 78
 - production, 75–81
 - reaction rate *vs.* other
 - polyisocyanates, 116
 - volumes, 63, 64, 73
- metathesis, 58
- modulus, 14, 114–15, 139–43, 145,
 - 148–51, 173, 175, 191–2, 196–8,
 - 209, 218, 244, 261, 263, 300,
 - 304, 344
- molded flexible foam
 - choice of polyisocyanate, 215–16
 - crushing, 215
 - design considerations, 217
 - formulation, 213–17
 - high resilience foams, 213, 215
 - hot *vs.* cold mold, 213, 215
 - market drivers, 246–7
 - mold filling, 216
 - preparation, 213–17
 - regional preferences, 217, 246–8
 - vs.* slabstock foams, 213
 - trends, 249–52
- monol, 17, 318
 - calculation of, 17
 - effect of counterion, 17, 24
 - effect on functionality, 19
 - mechanism, 19
 - vinyl termination, 16
- Mooney-Rivlin equation, 145
- nitration of toluene, 66–7
- non-isocyanate routes to polyurethanes,
 - 392–406
 - publication/patent activity, 394–5
 - reactions of amines with CO₂ and alcohol, 400–403
 - reactions of aziridine with CO₂,
 - 398–9
 - reactions of carbamates, 403–4
 - reactions of cyclic carbonates and polyamines, 394–5, 397–400
 - reactions of hydroxamic acids, 404–6
 - reactions of hydroxylamines, 406
 - regulatory drivers, 393
 - via isocyanate preconversion, 395, 396

- non-phosgene routes to isocyanates
 - Curtius rearrangement, 72–3
 - reductive carbonylation, 71–2
 - thermolysis of urethane, 70–71
- nuclear magnetic resonance spectroscopy (NMR), 199–202
 - application to polyurethanes, 200–202
 - limitations, 200
 - magic angle spinning (MAS), 200
- nucleation and growth, 134–7, 169
- optical microscopy, 169–70
 - phase contrast imaging, 169
- Organization for Economic Cooperation and Development (OECD) 383
- Ostwald ripening, 137
- oxirane(s), 12, 16, 20
- ozone depletion potential (ODP), 281–2
- ozonolysis, 55–6
- percolation equation, 142
- percolation threshold, 139–40, 145–6
- PHD polyols, 48, 50–51
- phase separation, 9, 86, 90, 129–38, 145–6, 149, 168, 175, 186, 221, 229, 232, 250, 313, 317–19, 345, 360, 400
- phosgene, 65
- phosgenation
 - gas-phase, 69
 - of hexane diisocyanate, 84
 - of H₁₂MDI, 86
 - of isophorone diisocyanate, 84–6
 - of methylene bisphenyldiamine, 78, 81
 - of toluene dianiline, 68–9
- PIPA polyols, 48, 51–3
- polyamide, 84, 345, 346
 - structure, 4
- polyanilides, 385
- polybutadiene polyol, 13
- ε-polycaprolactone, 33–5, 46, 131, 182, 320, 346, 383–4
- polycarbonate polyols, 13
 - preparation, 42–4
 - structure/applications, 46
 - standard tests, 161
- polyester
 - adipate polyester(s), 34, 46, 182, 302, 305, 344
 - aliphatic, 28, 34
 - aromatic, 28, 34–42
 - crystallization, 34–5
 - hydrolysis, 12
 - phthalate polyesters, 30, 32, 34, 36, 38, 40–42, 162
 - polymerization, 29, 32–9
 - polyol, 4, 11, 13
 - standard tests, 161
 - structure, 4, 30–31
 - succinate polyesters, 32, 34, 182, 183
- polyether
 - ceiling temperature, 12
 - initiators, 18
 - polyol, 2, 4, 11–28, 32, 36, 48, 90, 163, 228, 290, 301–2, 304, 317–19, 324, 328, 340–341, 344, 346, 354, 356, 380, 383, 400
 - standard tests, 161
- polyethylene glycol, 15
- polyisocyanurate foams
 - and CA regulation, 265
 - catalysis, 261
 - cell structure, 262
 - comparison to other construction foams, 265
 - inherent flame retardance, 261
 - formulation and properties, 262
 - insulation values, 263–4
 - panel structure, 262
 - production, 264
 - sandwich board, 261–2
- polylactic acid, 383–4
- polypropylene glycol, 15
- polyurethane
 - formation of, 128–37, 166–7
 - phase separation mechanism, 134–7
 - polydispersity, 128–30, 130
 - structure, 4
- polyurethane dispersion (PUD) adhesive, 346–49
 - formulation and properties, 350
 - growth, 347
 - non-reactive vs. reactive, 348
 - preparation, 347–49
- polyurethane dispersion (PUD) coatings
 - hybrid formulations and properties, 362–3
 - laboratory method for production and properties, 361–2
- Porod analysis *see* small angle x-ray scattering

- pour-in-place (PIP) foams
 - applications, 271
 - cavity filling, 271–2
 - contrast to other foams, 270–272
 - formulations and properties, 273
 - insulation properties, 272
 - lance withdrawal technique, 272
 - water-blown, 272
- powder coatings, 119, 364–8
 - blocked isocyanates, 365–7
 - formulation and properties, 367–8
 - preparation, 365
- prepolymers, 59–61
 - characteristics, 311
 - and elastic fibers, 324–6
 - low-free *vs.* stripped, 309–12
 - market size, 312
 - preparation, 61, 309
 - quasi-prepolymer *vs.* full prepolymer, 301, 311, 313–14
 - regional preferences, 309
 - structure, 60, 310, 311
- 1,2 propylene oxide, 12–14
- pultrusion, 321
- PTMEG, 11, 25–27, 317–18, 324, 326, 382
- quasi-prepolymer, 59, 301–2, 309, 311, 312
- radiation (Rad) cure adhesive, 339, 340
- radiation (Rad) cure coatings, 363–4
 - applications, 363
 - formulation and properties, 364–5
 - initiators, 364
- Regulation, Evaluation, Authorization, and Restriction of Chemicals (REACH), 251
- reaction induced phase separation, 9, 129, 134–7, 219
- reaction injection molding (RIM), 299, 320–323
 - automotive applications, 321
 - comparison to RTM and SMC, 321–2
 - formulation and properties, 322
 - geographical segmentation, 323
 - production, 321
 - R-RIM, S-RIM, LFI-PUR, 320–321
 - trends, 323
 - windmill parts, 323
- reactive hot melt adhesive, 341, 345–6
 - formulation and properties, 346
- reaction rates, 106–7, 118
- recycle, 237
- renewable feedstocks, 8, 237 *see also* seed-oil derived polyols
- resonance frequency, 251
- rigid foams, 255–90 *see also* appliance foams; construction foams; froth foams; polyisocyanurate foams; pour-in-place (PIP); spray; thermal insulation
 - commercial considerations, 257
 - construction foams *vs.* appliance foams, 260
 - markets, 255–60, 274
 - standard tests, 275
 - trends, 287–90
- ring-opening polymerization, 33
- run-flat tires, 323
- scanning electron microscopy (SEM), 169–72, 262
- seed-oil derived polyols, 53–9, 237, 290
 - fatty acid structure, 54
 - in furniture, 241, 251
 - preparation, 55–9
 - seed-oil composition, 54
- Simha-Boyer rule, 154
- slabstock flexible foams, 34, 213, 215, 217
 - automotive, 246
 - bedding, 241–2
 - density, 210–211
 - formulation, 210–212
 - furniture, 239
 - high resilience, 211–12
 - market drivers, 246
 - production, 208–12
 - scorch, 209
- slurry, 68
- small angle x-ray scattering (SAXS), 135, 168, 184–8
- solubility parameter, 131, 133
 - of common solvents, 387
- solvent borne coatings
 - design criteria, 360–361
 - formulation and properties, 361
- spandex *see* elastic fiber
- spinodal phase separation, 135–6

- spray foams, 36, 265–7
 - advantages over board insulations, 265, 267
 - formulation development, 265–6
 - formulations and properties, 267
 - factors affecting quality, 265
 - tests, 265
- Stepan Corporation, 32
- stress amplification factor, 145, 147
- stress-strain behavior, 143–9
- styrene-acrylonitrile (SAN), 48–9, 51, 215
- support factor *see* comfort factor
- surfactants and surfactancy, 212, 224–5, 226–8
 - efficiency, 228
 - role in foaming, 226, 228
 - silicone, 226–8
- systems house(s), 240, 247, 308, 316, 350, 359, 370
- tensile testing, 189–95
 - extensometer, 194
 - fixtures, 191, 193–4
 - test standards, 190
- tetrahydrofuran, 11
 - production, 15
- thermal insulation, 36, 277, 280, 284–7
 - gas conductivity, 287–8
 - K-factor, 284–5
 - Knudsen effect, 287, 290
 - Knudsen number, 287
- thermoplastic elastomers (TPU)
 - vs.* cast elastomers, 294–5, 314–15
 - catalysts, 317
 - commercial relationships, 315–16
 - comparison of elastomers from polyether and polyester soft segments, 319
 - comparison to other elastomers, 319
 - design, 318–19
 - footwear, 300–301
 - formulations and properties, 320
 - markets, 315–16
 - production, 315, 317
- thermoplastic olefin elastomers (TPOs), 321
- thermoplastic rubber (TPR), 300, 306–7
- time-temperature superposition, 196
- toluene, 63, 65
- toluene diisocyanates (TDI), 50, 51, 53, 62
 - growth, 63
 - photooxidation, 82–3
 - preparation, 65–9
 - reaction rate by ring position, 115–16
 - volumes, 63, 64
- TPU *see* thermoplastic elastomers
- transportation, 245–52
 - commercial structure, 249
 - formulations, 247, 248
 - markets, 246–7, 249
 - patent trends, 249–51
 - vibration and comfort, 250–251
- triglycerides, 55
- transmission electron microscopy (TEM), 169, 172
 - phase contrast agents, 172
- trimer(ization) of aliphatic isocyanates, 61, 77, 86–7, 111–12, 119–21, 180, 261, 265, 359–60, 367, 369
 - regulation of, 393
- United States and Canada
 - flexible foam consumption, 236–8
 - prepolymer preferences, 309
 - rigid foam market, 255–6, 259
 - seating foam preferences, 246
- United States Department of Energy, 277
- United States Environmental Protection Agency (USEPA), 237, 392–3
- United States Occupational Health and Safety Administration (OSHA), 393
- urea
 - activation energy of formation, 117
 - formation, 116–17
 - structure, 4
- urethane
 - effect of solvent on reaction, 116
 - heat of reaction, 113
 - reversion, 113–14, 198
 - reversion temperatures, 113
- uretidione, 79, 81, 119, 367
- uretonimine, 120–122, 301
- viscoelastic foams, 241–5
 - design concepts, 243–4
 - formulations, 245
 - glass transition, 244
 - production, 243–4

- Wanhua Group, 257, 315
- wide angle x-ray scattering (WAXS), 181–3
- wound dressings, 380–382
 - applications, 381–2
 - design criteria, 381–2
 - electrospray preparation, 382
 - occlusive vs. non-occlusive, 381
 - volumes, 380
- xylene, 32, 46, 64
- zinc catalysis, 21, 22, 307, 367

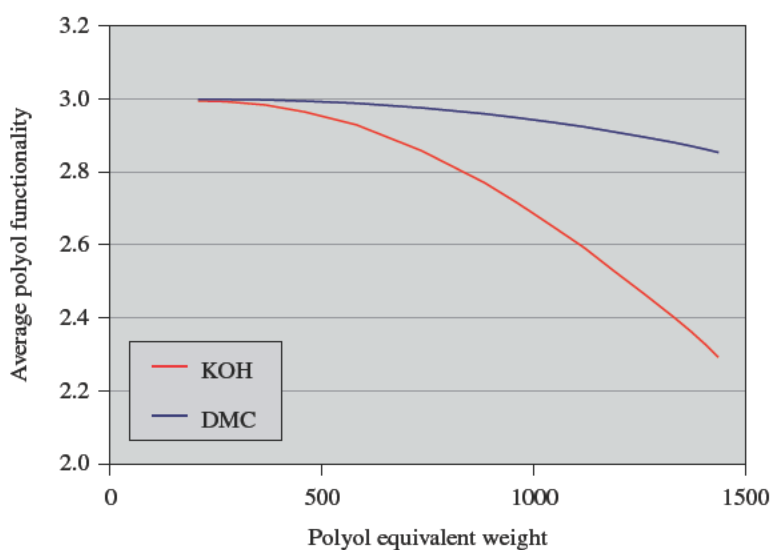


FIGURE 2.14 Difference of measured polyol functionality attained by KOH and DMC catalysis for a triol of variable equivalent weight. The difference becomes appreciable at higher equivalent weights as the number of end-groups decreases. Reprinted with permission from Ref. 37. © John Wiley & Sons, Inc.

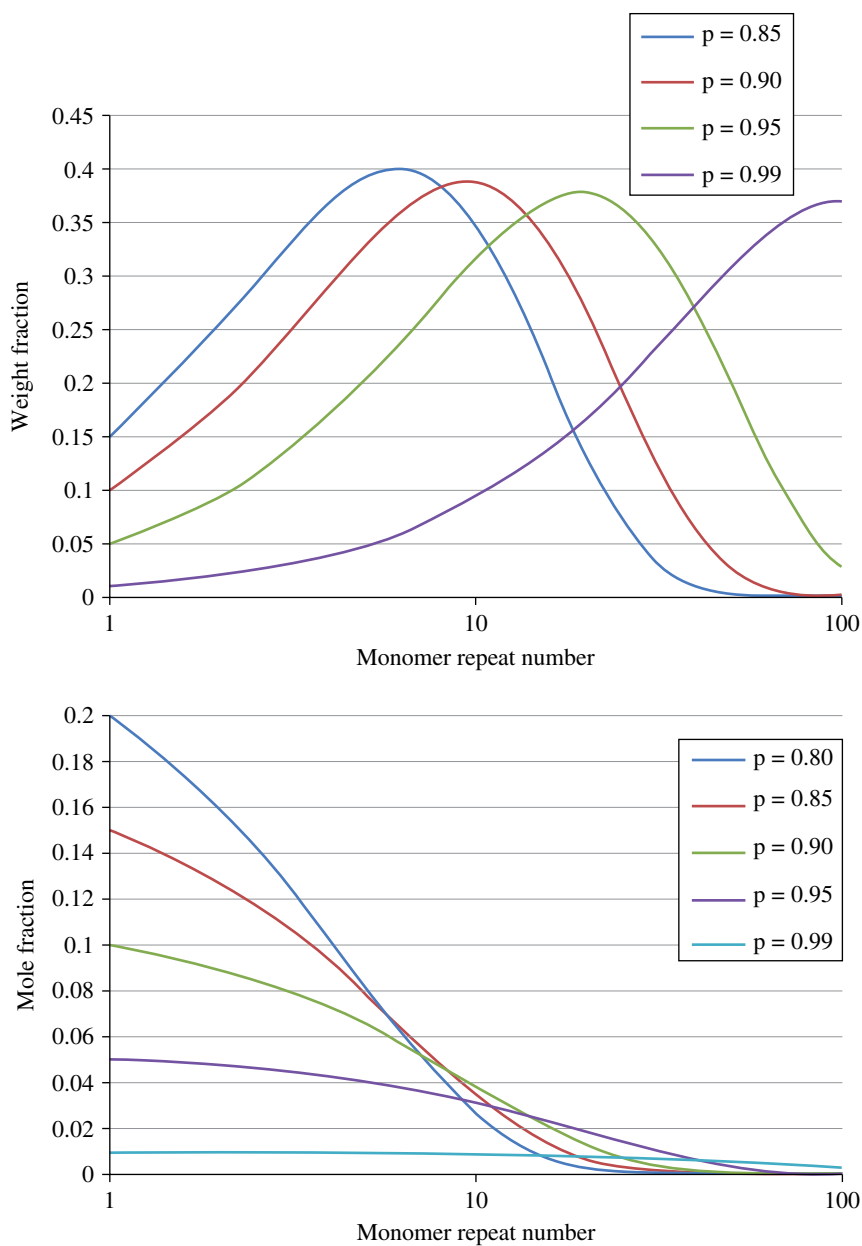


FIGURE 2.25 Weight and number average distributions of oligomer sizes present in a polyester synthesis based on the Flory-Schultz distribution.

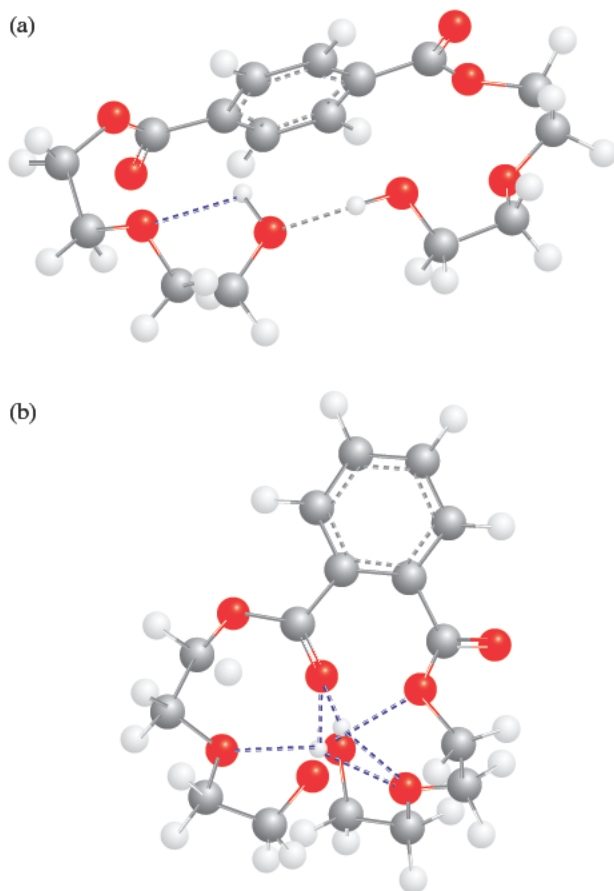


FIGURE 2.28 Comparison of lowest energy conformations of aromatic polyester polyol from (a) terephthalic acid and (b) orthophthalic acid (or phthalic anhydride) and DEG. The free volume requirement of the ortho positional substitution is much higher which may account for much of the viscosity difference between polyols made with the different co-monomers.

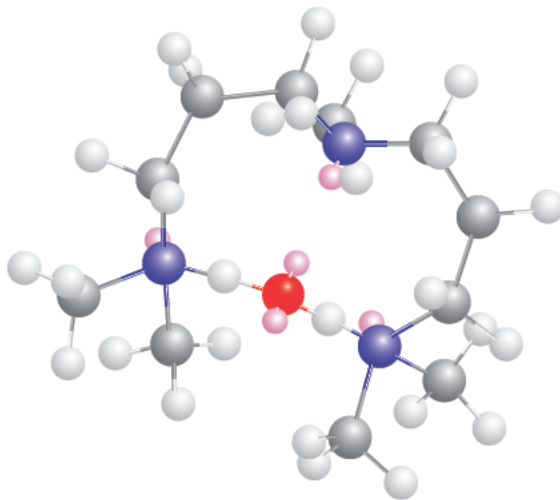


FIGURE 3.8 Energy minimized interaction between water and pentamethylene dipropyleneetriamine demonstrating the favorable water interactions that result in good blow catalyst properties (light red surfaces indicate non-bonding electron pairs, red is oxygen, and blue is nitrogen).

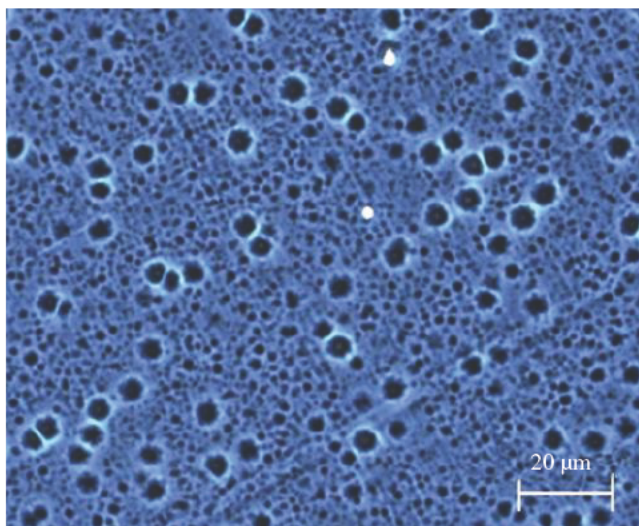


FIGURE 5.4 Phase contrast optical microscopy of a cast polyurethane elastomer—dark areas are hard segment. See Figure 5.6 for comparative image quality and information content versus TEM. Image courtesy of Robert Cieslinski and Justin Virgili.

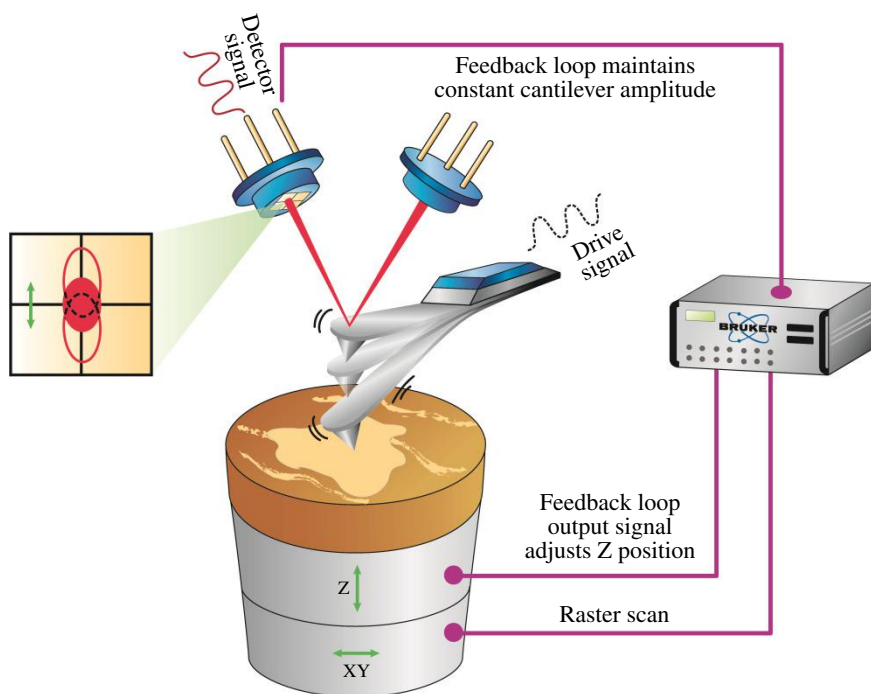


FIGURE 5.7 Simplified illustration showing sample and signal detection controls for a tapping mode atomic force microscope and the appearance of a working instrument. Images courtesy of Bruker Nano-Surface.

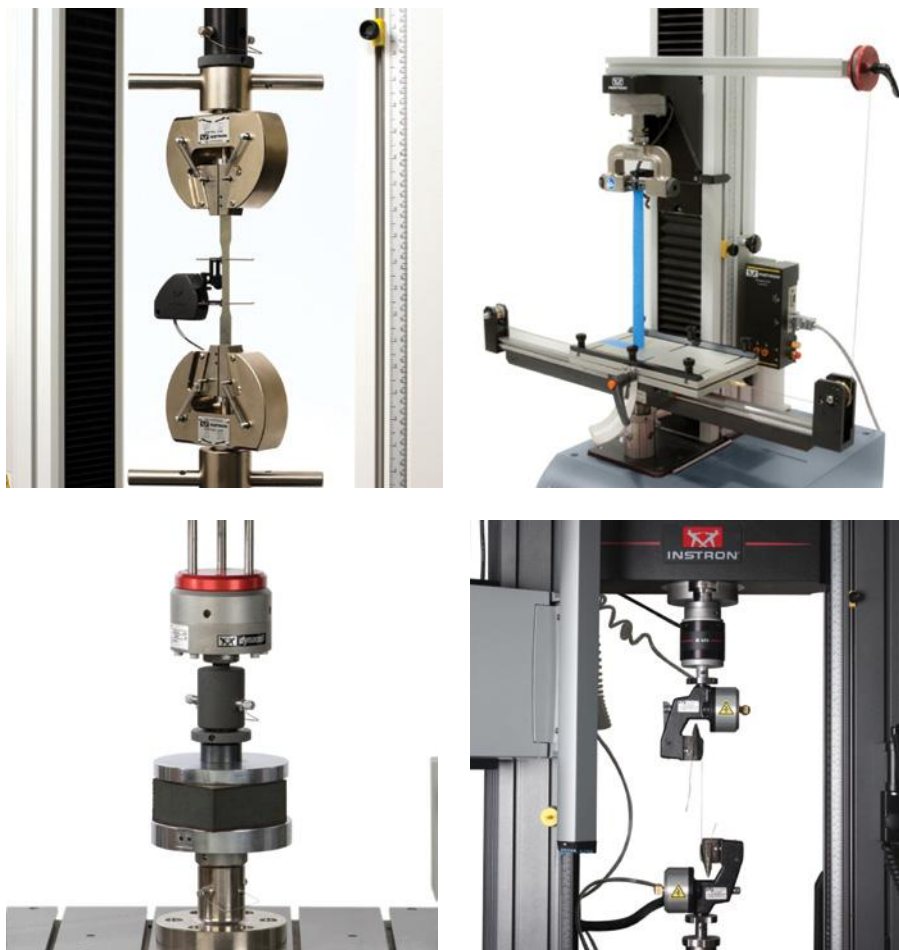


FIGURE 5.22 Useful fixtures for mechanical testing of polyurethanes. Clockwise from upper left: standard tensile fixture for testing plastics, 90° peel test fixture, cord and yarn fixture, and compression fixture. Images courtesy of Instron®.

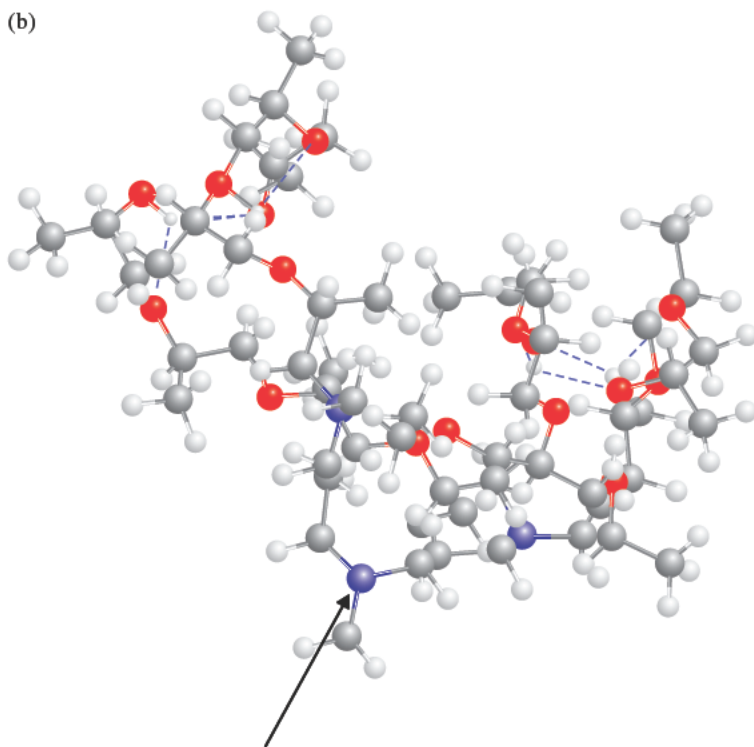
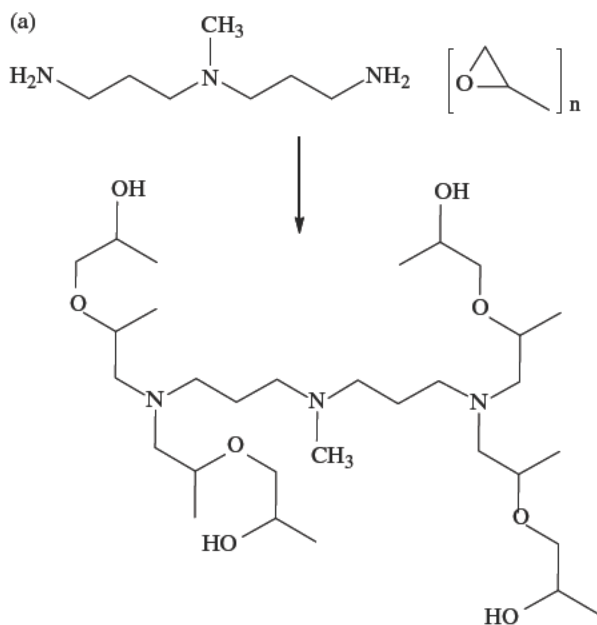


FIGURE 6.8 (a) Example reaction for making a catalytic polyol. The reaction is usually base catalyzed. (b) Energy minimized space filling structure for a reactive catalytic polyol. The arrow indicates the position of the central catalytic tertiary amines. The alkoxyated aminines are usually much less catalytic due primarily to steric hindrance as well potentially electrostatic factors associated with local ether associations.

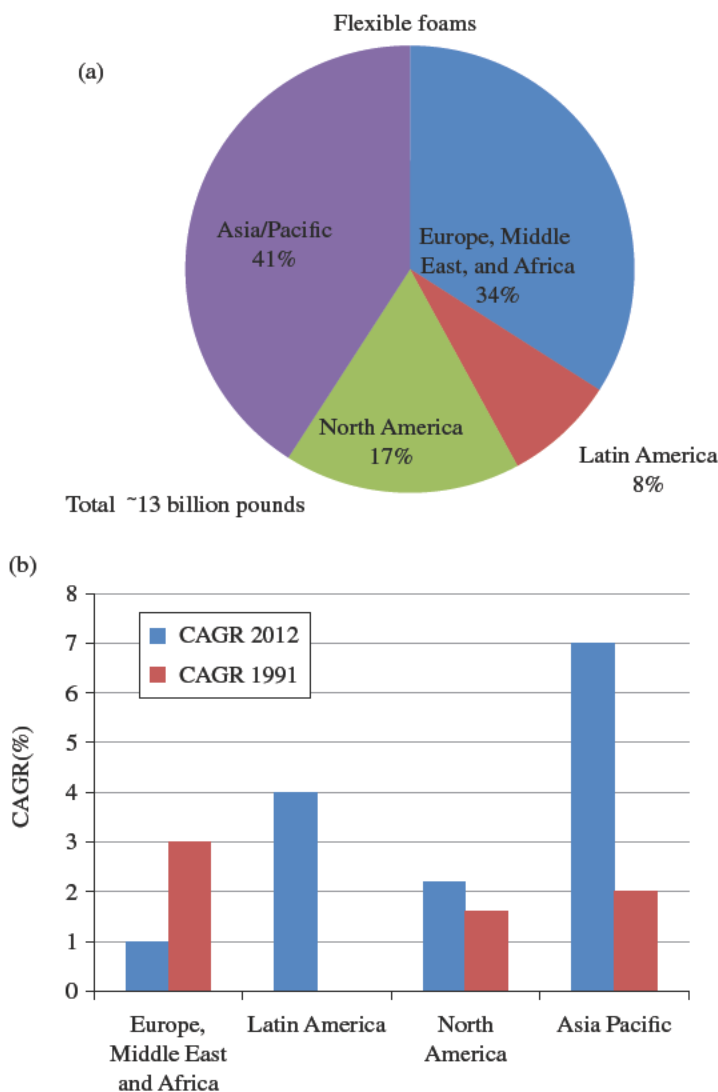


FIGURE 7.1 Approximate volume breakdown for the production (a) of polyurethane flexible foams by geographical region for the year 2012 and (b) the compound annual growth rate of flexible polyurethane foam production for the years 1991 and 2012. History can be a guide for the future, but extrapolation becomes less reliable the greater the distance from the reference year.

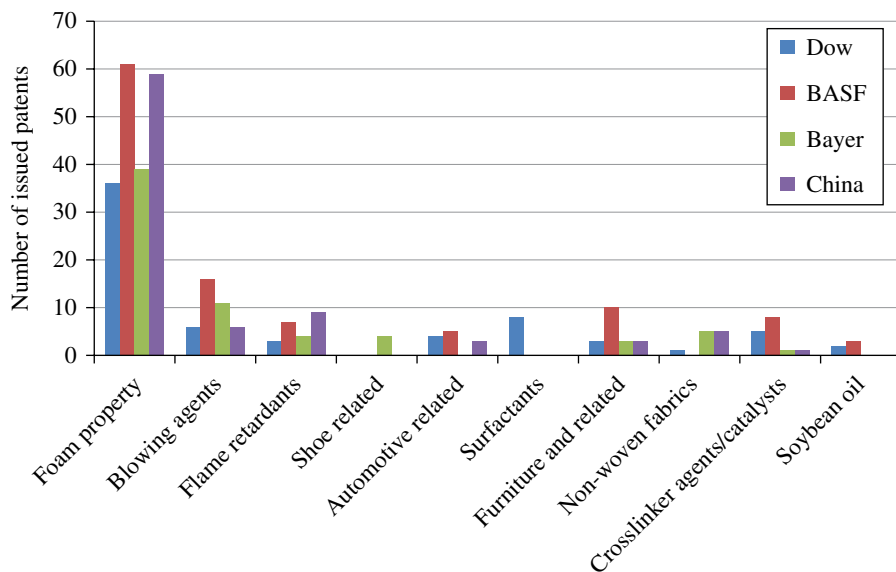


FIGURE 7.11 Patent activities within flexible polyurethane foam category of several large polyurethane market servicers and the patents filed in the Chinese language for the years 2000–2013 over the years 2000–2013.

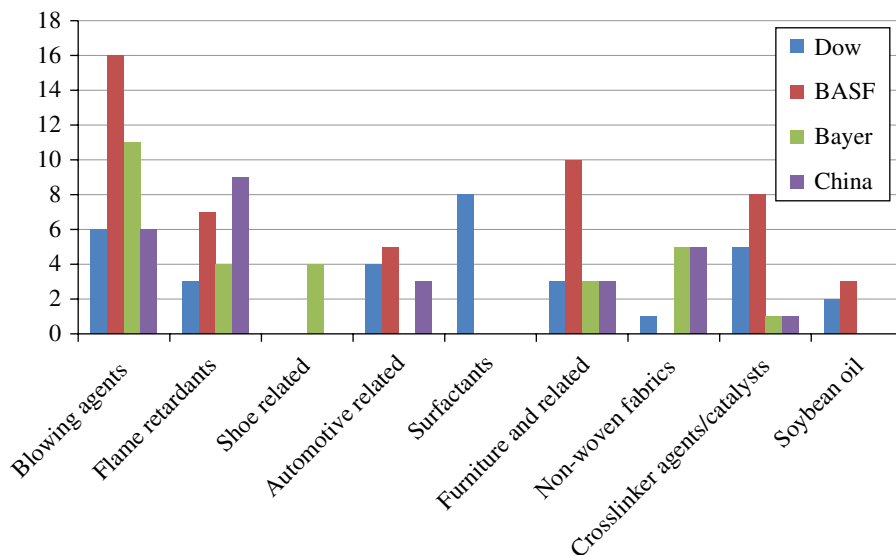


FIGURE 7.12 Data of Figure 7.9 with “Foam property” category removed to improve visualization of more specific subjects.



FIGURE 8.16 Form (left) of a purchased froth foam system and function (right) of a froth system in use.

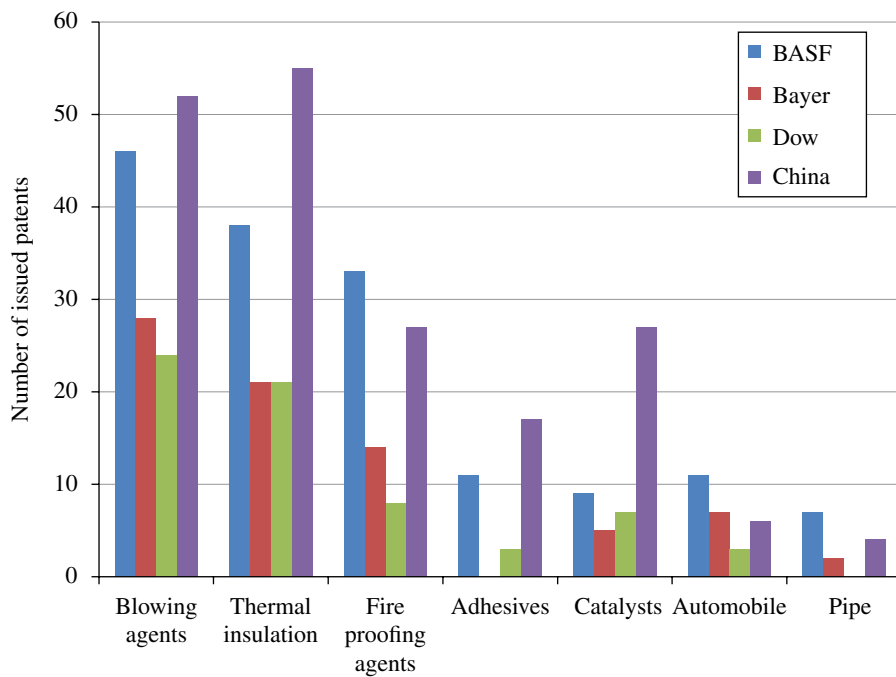


FIGURE 8.24 Patent activity of three large polyurethane chemical producers in the field of rigid foams by topic.

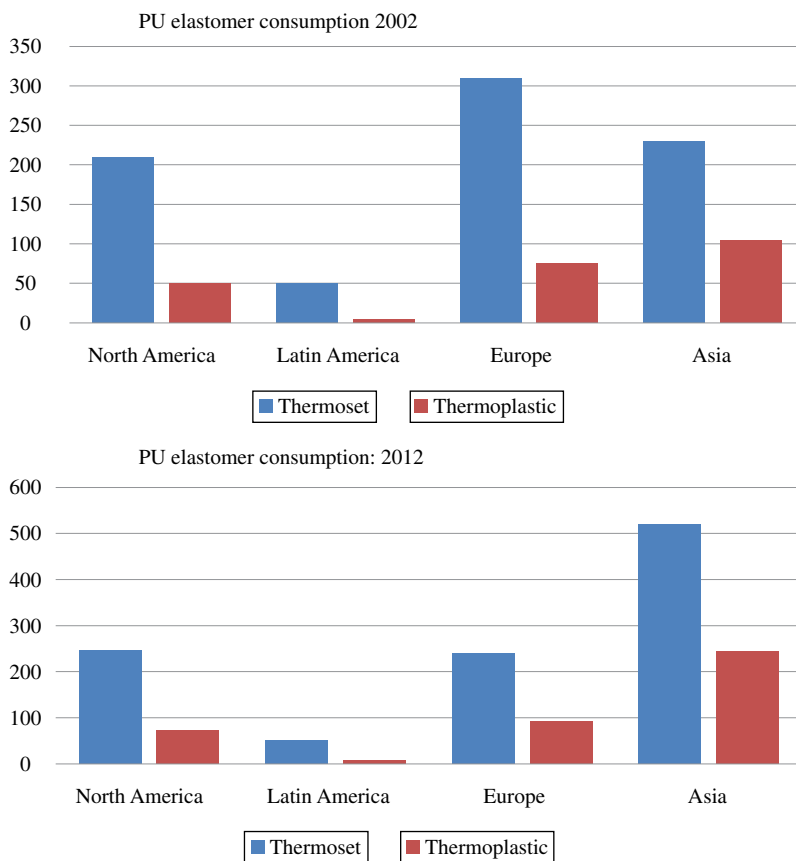


FIGURE 9.5 Regional industrial consumption of PU elastomers for the years 2002 and 2012 reflecting the migration of thermosetting elastomers, especially for shoe soles, to Asia. Units are MM lbs.

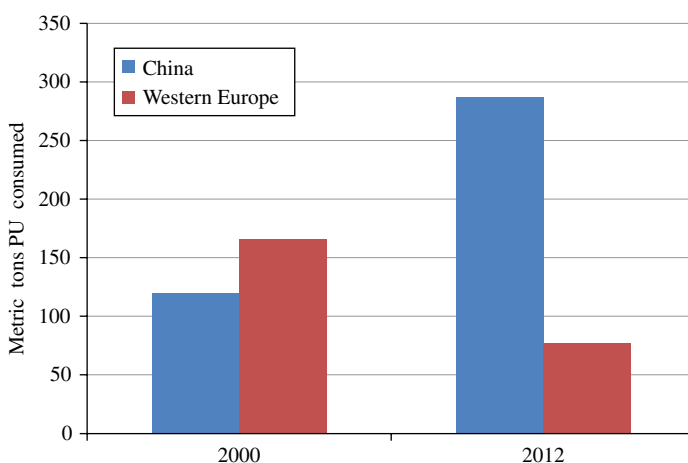


FIGURE 9.7 Consumption of microcellular polyurethane elastomer primarily used in footwear applications comparing data for Western Europe and China for the years 2000 and 2012 [9].

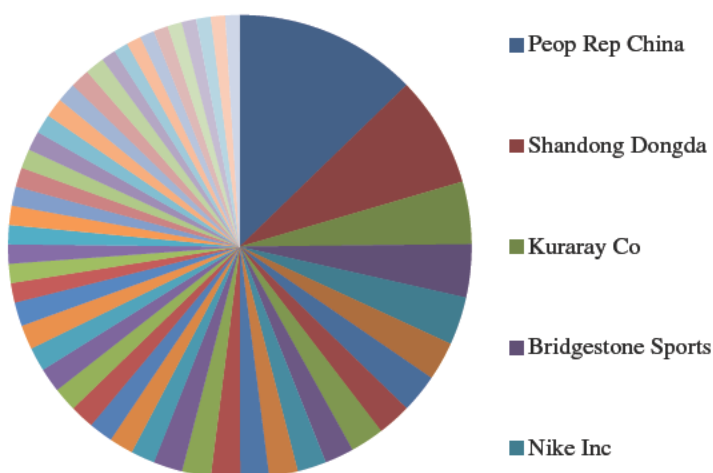


FIGURE 9.28 Pie chart of all patents filed from 2010 to 2013 relative to the activity of the top five assignees. The top five account for about 25% of all polyurethane elastomer patents filed.

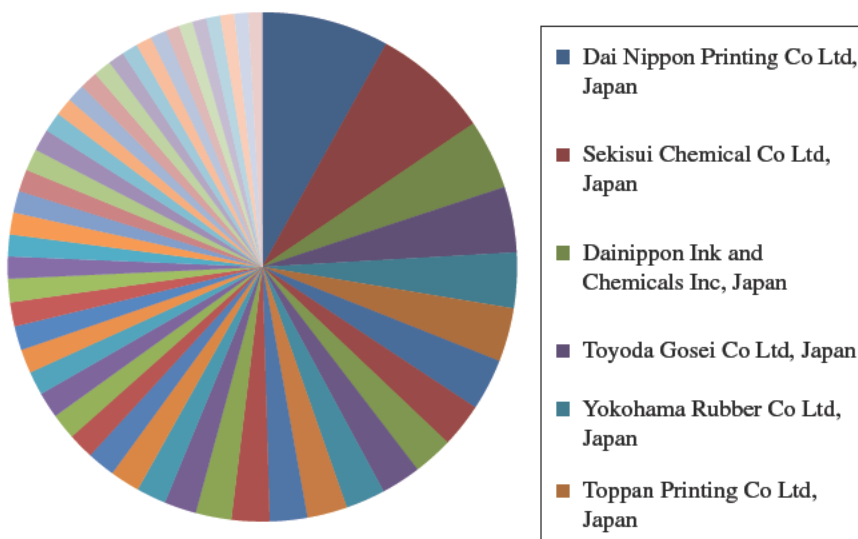


FIGURE 10.13 Global patent activity for polyurethane adhesives for companies having *more than 5 patents*. The top five patenting companies (by number of publications are indicated). The graph shows the large number of formulators and manufacturers active in the competitive marketplace.

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